OIL COLOURS AND PRINTERS' INKS

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A PRACTICAL HANDBOOK

TREATING OF

LINSEED OIL, BOILED OIL, PAINTS, ARTISTS' COLOURS, LAMPBLACK AND PRINTERS' INKS, BLACK AND COLOURED.

BY

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PREFACE TO GERMAN EDITION.

HAVING been engaged uninterruptedly for a series o years in the manufacture of varnishes, pigments an coloured printing inks, I may well feel impelled, witho presumption, to write a book upon these subjects, th more so as literature is somewhat deficient with rega to them.

My book, in addition to distinct information wit regard to linseed oil, the chief raw material, its purific tion and bleaching for making varnishes and pigment contains short dissertations on the theory of drying o and of the pigments that can be used with it, and th chief adulterations. I have thought that any descri tion of pigment manufacture, with the exception lampblack, to which I have devoted a special chapte would be superfluous, as excellent and copious boo on the subject have appeared.

Attention has been chiefly given to the manufactu of pigments, their mixing and grinding, and to th manufacture of printers' varnishes and coloured ink including all the latest patented products. The secti dealing with artists' colours is quite new and h appeared in no other work of this kind. I trust th part of my work will meet with a good reception trade circles, and will establish my reputation as expert in matters concerning this special industry.

L. E. ANDÉS.

Vienna, 1889.

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CHAPTER I.

INTRODUCTION.

THE great technical progress that has been made in every direction has naturally made itself felt in the manufacture of pigments for all purposes. This has been especially the case during the last forty years.

Before that time the industry was in a very primitive state. Pigments were rubbed up by hand on a glass or stone plate by means of a muller. This method certainly yielded finely divided colours, but the output per man was so small that in large factories more hands were employed in grinding the colours than in making them. Artists, too, looked upon the labour of grinding their own colours as a most important necessity. In this way only were they always able to use fresh pigments, and were not obliged to struggle with a medium which through long keeping had become unmanageable. In view of the fact that artists use a comparatively small amount of pigment, they were probably quite right to take this trouble at the period, but with house-painters and others who use large quantities the case was very different. With the increase of demand the pigment-makers found their stone and muller method utterly inadequate to cope with requirements, and the invention and introduction of machinery inevitably followed.

Printers' colours underwent the same evolution. Formerly the printer always prepared them himself. On fine days the printing-office staff went out into the garden or the fields

and rigged up their boiling pot. Then the assistants had a festival, culminating in roasting bread in the hot linseed oil and eating it. The boiled oil was then mixed with the pigment and the finished ink was taken home. What would a modern printer say if asked to use such a lumpy mixture? Here then, too, machinery had to be introduced before a product which made modern printing possible could be produced. The substitution of power-driven printing machines for hand presses had a great deal to do with producing this change.

That the progress in colour manufacture has not been solely a question of grinding is easily understood, and we have s..ing and mixing machinery to describe, and to these a special part of the book is devoted.

As a vehicle for oil-colours linseed oil has always been the mainstay of the industry, and we also use poppy oil and nut oil in the manufacture of artists' colours. Of the other drying oils—hemp, sunflower, cotton, grape-seed, tobacco-seed, dodder, croton, castor, madia, etc.—hemp oil is used locally, in Galicia and Russia. The bankul oil of *Aleurites triloba* might advantageously be imported from Martinique, Guadeloupe, New Caledonia, Tahiti, Guiana, and Reunion, and used for pigments and varnishes, but so far no quantities worth mentioning have been brought to Europe.

The siccative properties of linseed oil are developed either with reducible metallic oxides or other bodies rich in oxygen, or, still better, by means of oxygen itself. The oil may also be purified or bleached for colour mixing. The artist in oils should only use linseed, poppy, or nut oil that has been nature bleached, especially for delicate shades, but manufacturers have already gone so far as to use cotton-seed oil in manufacturing even comparatively high-priced artists' colours.

The purification and bleaching of linseed oil, and its boiling are matters of great importance in colour preparation, and

shall be described with corresponding minuteness. For the printer, linseed oil and lampblack are the most important raw materials, and the practice of centuries has shown that a pure, clear, long-stocked linseed oil is the only suitable oil for his use. This, then, the modern manufacturer must remember and pay heed to.

The number of pigments used for painting of all kinds and by printers has steadily increased with the lapse of time, and although many are now offered of excellent appearance which fall short of the claims put forward on their behalf, yet experience will soon teach the user how to make his choice. This book will enable the colour-maker to improve his somewhat defective knowledge, and to give him the certainty in judgment that he most certainly requires.

Although in our industry the preparation of dry colours is only occasionally undertaken by the manufacturer of mixed paints, yet in all cases the maker of printers' ink should produce his own lampblack, and the methods of doing so are detailed in a special part of this work.

It is unnecessary to dwell on the fact that a time so rich in inventions as the present has not stood still as regards colour manufacture, and that many proposals have been and are still being made to replace drying oils as vehicles for pigments by cheaper or better substitutes. I feel myself called upon, however, to remark in this connection that no substitute hitherto suggested is superior to the drying oils, and that at present a good paint, whether for artistic, printing or general purposes, can only be made with a drying oil.

CHAPTER II.

LINSEED OIL.

LINSEED oil is made from the seeds of the flax plant, *Linum usitatissimum*. The plant is largely cultivated in Holland, Russia, Austria, Germany and France. These European sources of supply are, however, inadequate for the enormous consumption, and most of the linseed oil of commerce is now made from East Indian seed, which comes in cargoes to Holland and England, where the oil is extracted. The native place of the flax plant is Asia, and it was known to the ancients, who made linen from it, as is proved by microscopical examination of mummy-cloths.

The oil is obtained:—

1. By cold pressure, if the oil is to be used as an article of food.

2. By hot pressing for technical purposes only, as the oil obtained has a disagreeable taste.

3. By extraction.

Each method gives a different yield of oil.

Cold pressing gives 20-21 per cent.

Hot „ „ 27-28 „

Extraction „ 32-33 „

Oil from fresh seeds is mucilaginous and turbid, the seeds therefore are stocked for from two to six months before pressing.

The seeds are then broken up by stamps, rollers, or in a pugmill, and next heated by steam or over the fire in suitable vessels. Various advantages are secured by heating the seeds. The oil becomes thinner, and flows out more easily

under the pressure. The yield is increased, the albuminous bodies in the seed are coagulated and the mucilaginous substances are dried up. There is, however, the disadvantage that the hot oil dissolves colouring matter and extractives with a disagreeable taste out of the residue of the seeds. Hence, as we have already said, hot pressed linseed oil is used only for technical purposes.

The pressure is applied with hydraulic or wedge-presses and either horizontally or vertically. All large oil factories now use hydraulic presses.

The production of oil by pressure has been frequently described and the apparatus is well known, but as the extraction process is less familiar I will describe it more fully. Deite says in his *Technologie der Fette und Oele* :—

"Even by the use of the greatest pressures at our command it is impossible to press all the oil out of the seeds. It is this residual oil that gives value to the press-cakes, which contain about 10 per cent. of it. To get the full yield from the seeds, solvents must be used. Schrotter showed the method of manufacturing bisulphide of carbon in 1838, and Jesse Fisher, of Birmingham, the introducer of the employment of the bisulphide industrially, first used it for extracting linseed oil in 1843. Deiss and Sufferth of Brunswick followed in Fisher's footsteps. Besides bisulphide of carbon other solvents are available, especially petroleum-ether, benzole, canadol, etc., introduced by Vohl Richardson and Hirzel."

Lampadius, the discoverer of bisulphide of carbon in 1796, made it by the method still used, *viz.*, passing sulphur vapour over red-hot carbon, and oil factories using it always make their own. The apparatuses in which the bisulphide is put to the linseed are all alike in the main features of their action, including the recovery of the bisulphide of distillation. The bisulphide passes vertically through the seeds, but sometimes upwards and sometimes downwards. The bisulphide can be added to the seeds themselves, previously crushed as above

described, and then dried, or may be used to extract the residual oil from the press-cakes. For this purpose the press-cakes are ground up. Air-tight iron cylinders are used for the extraction.

As soon as carbon bisulphide had been introduced for oil extraction a controversy arose as to its merits. The farmer lamented the loss of oil-cake for fodder. The cows would not eat the sulphur-smelling residues from the extraction process. The oil-dealer complained of the disagreeable smell and taste of the oil, the soap-boiler of the odour the oil communicated to his soap, and the painter because the oil blackened white lead, whether it was stirred up with that pigment or applied to it in the form of another paint.

Chemists complained that colouring matter was dissolved by the bisulphide and also a resinous sticky body, which favoured absorption of oxygen, and caused rapid resinification and rancidity of the oil. The oil also contained seed meal which unfitted it for many purposes. All these things combined killed the extraction process. The existing factories did not prosper, and most of them stopped altogether. Just at this time, moreover, the opening out of the petroleum industry in America caused a use to be sought for petroleum-ether, and it was speedily adopted instead of bisulphide of carbon for oil extraction.

A light petroleum-ether boiling at 60° C. enables us to get a very pure oil from seeds as it does not dissolve resins, whence Vohl called it canadol. Raw canadol itself contains sulphur, and must therefore be treated with bichromate and sulphuric acid, and then rectified.

Opinions as regards the comparative merits of canadol and bisulphide of carbon for extraction purposes were formerly very divided. Now, when the manufacture of the bisulphide has been so improved that repeated rectification gives us a product which will extract oil of perfect purity, and with an agreeable smell, and when the cost of producing the bisul-

phide is so low that it can compete with canadol, the question which of the two is to be preferred comes up, and must be considered. The answer is that when the oil is to be used for food or for perfumery extraction with canadol is to be preferred. For all other purposes the choice must be determined by the current market prices of the two solvents. In favour of bisulphide of carbon it must be mentioned that it is more convenient to use, as it is employed cold for extraction, while canadol must be boiling. Hence the apparatus required is less expensive in the case of bisulphide. Again, very old seeds are not perfectly exhausted of oil by canadol, whereas the full yield is obtained with carbon bisulphide.

Practice has now got rid of all the troubles attending the use of bisulphide of carbon. The residues have no longer the least smell, and have long since regained favour as fodder. The result has been that the factories of bisulphide existing when the improvement in the manufacture was made were soon unable to cope with the demand, and during the last ten years the output of bisulphide and its use for oil extraction have greatly increased. It is found that it is cheaper to extract the oil than to press it out, and that it can be done with a less outlay of capital. The oil works using the extraction process have propitiated the farmers by abandonment of complete exhaustion of the oil, and this step has by the way almost quadrupled the output of the factories.

Cold-pressed oil is nearly colourless, having only a very pale yellow tint, while hot-pressed oil is distinctly yellow, or even brown. The dissolved-out oil is of a very pale yellow. The taste of linseed oil differs from that of the non-drying oils, and is a characteristic bitter with a rough after-taste. The smell of the oil is also peculiar, and Mulder does not think it due solely to volatile fatty acids, such as butyric, valerianic and caproic.

Linseed oil does not freeze until far below zero C. Gusserow says that it will freeze at −16° C. if kept several days at

that temperature. Saussure says – 27½° C., and I would put its freezing point still lower, as I have never succeeded in getting solid linseed oil at temperatures of – 28 or – 29° C. It dissolves in sixteen times its weight of ether and in forty times its weight of cold alcohol, or in five times its weight of boiling alcohol. With oil of turpentine it mixes in all proportions. Its specific gravity is:—

·9395 at 12° C.
·9300 at 25° C.
·9125 at 50° C.
·8815 at 94° C.

Linseed oil boils at 130° C. On the oil-balance it should show 30°, but the indications of the instrument are not altogether trustworthy. At from 360 to 400° C. the stinking vapours which began to come off at 210° will catch fire, and burn with a red flame and with much smoke.

Fresh linseed oil is saponifiable, and forms a yellow soft soap with soda. A solution of this soap treated with hydrochloric acid gives a fluid supernatant layer, which forms crystals of stearic and palmitic acid on cooling.

By boiling linseed oil in the air we get first boiled oil, and by further heating to a high temperature a tough mass which will not make a greasy mark on paper. It is usual to set fire to the fumes, but this is not indispensable. If heated beyond a certain point linseed oil loses its drying power, and becomes sticky and elastic. To remain drying it must be heated till the linoleine begins to decompose. Among the first products which the heat volatilises are derivatives of oleine, myristine and palmitine.

When linseed oil has been heated to a tough mass that mass will become solider if boiled in dilute nitric acid. The acid promotes the separation of the linoleic acid from the glycerine, so that the smell of acrolein becomes noticeable. Finally, according to Jones, the mass becomes a sort of india-rubber, and is no longer sticky to the touch, and no

longer fusible. It is, however, still soluble in bisulphide of carbon to an emulsion. If this india-rubbery mass is boiled in concentrated potash lye, it combines with it, but is not dissolved. The compound is decomposed by acids, setting the india-rubbery substance free again. In alcohol-containing ether the india-rubbery substance swells up, and dissolves if more ether is added. It is reprecipitated by alcohol. In petroleum it swells up but does not dissolve. It will dissolve in a large quantity of oil of turpentine.

When linseed oil is dry distilled, we get as a distillate acrolein, partly oxidised to acrylic acid, salicylic acid, palmitic acid and myristic acid, with linoleic anhydride as a residue.

The ultimate composition of linseed oil is:—

	Cold pressed. per cent.	Hot pressed. per cent.
Carbon	78·11	75·27
Hydrogen	10·96	10·88
Oxygen	10·93	13·85

The oil is a mixture of linoleine $(C_{16}\ H_{25}\ O)_3\ C_3\ H_5\ O_3$, the glyceride of linoleic acid with oleine, palmitine and myristine, the linoleine forming about 81 per cent. Hence the saponification products are glycerine, linoleic acid and oleic or some allied acid, those of dry distillation being acids yielding sebacic acid, palmitic and myristic acids.

Linseed oil has more power than any other drying oil, absorbing oxygen from the atmosphere and on boiling with metallic oxides, whereby its composition is considerably altered and we get boiled oil.

Linseed oil is much adulterated, less, however, by the makers than by the middlemen. The adulterations used depend upon prices. They include rape, cotton and hemp oils, and also petroleum, fish oil, resin oil, colophony, etc.

Adulteration with fish oil is detected by stirring up ten parts of the oil to be tested with three of sulphuric acid. On

standing the oil and acid separate. If the oil contains fish oil it rises to the surface of a dark brown colour, while the acid below it is orange or brownish yellow. If the oil is pure, it is at first green, then a dirty yellowish green, while the acid assumes a purer yellow colour. This adulteration can also be detected by chlorine which bleaches pure linseed oil, but turns all animal fats first brown and finally black.

Adulteration with colophony and other resins may be detected by boiling the oil for a few minutes with S.V.R. of from ·88 to ·99 sp. gr., drawing off the solution when cold, and treating it with a solution of acetate of lead in alcohol. If the oil was pure, a turbidity results, but the presence of resins causes the appearance of a white curdy precipitate.

To detect resin oil, the senses of smell and taste are best relied upon. Even small quantities of resin oil can be recognised in linseed oil by the taste. A good plan is to rub a drop of the oil to be tested between the palms of the hands, for on separating them the smell of the resin oil can be detected. The following method is also said to be reliable. Mix at the ordinary temperature (not however below 15° C.) equal volumes of the linseed oil and nitric acid of sp. gr. 1·4. Shake the mixture well for half a minute, and then allow it to stand. When the oil and acid have separated we have the following colours:—

Nature of Sample.	Oil.	Acid.
Pure linseed oil	Pale cinnamon brown	Colourless.
Linseed oil + 5 per cent. resin oil	,, ,, ,,	Straw-yellow.
,, ,, + 12 ,, ,, ,,	Dark olive	Dark yellow.
,, ,, + 50 ,, ,, ,,	Blackish	Pale orange.

For accurate methods of testing linseed-oil adulteration with other vegetable oils, which only happens when their price relative to that of linseed oil makes it worth while, I refer the reader to Dr. Benedikt's *Analyse der Fette*, and will only give here Morawski and Demski's method for detecting unsaponifiable fats (petroleum and resin oil), because

it is with these that linseed oil is mostly adulterated at present.

The complete separation of the layers of liquid got by treating the soap with a volatile solvent is often difficult, but the following process enables it to be done always quickly and easily in the separating funnel. Ten grammes of the oil are treated with 50 c.c. of alcohol and a concentrated solution in water of 5 grammes of caustic potash. The whole is heated for half an hour with a reflux condenser. Then 50 c.c. of water are added, and the mass is cooled by standing the containing flask in cold water. The mass is then shaken up in the separating funnel with petroleum-ether. When the two liquids have separated the lower layer is drawn off as completely as possible. What remains in the funnel is washed repeatedly with water, but the washings are not added to what was first drawn off. Finally, the last washing is drawn off as completely as possible. As even with the greatest care drops of water accompany the ether when it is drawn off in its turn, it is not poured at once into the tared dish in which it is to be evaporated, but into another dry dish. It is then transferred thence to the tared dish, leaving the water behind adhering to the sides of the other dish. The first portion drawn off from the separating funnel is then treated with more ether, which after washing, etc., as above described, is also transferred to the tared dish.

To ascertain quickly whether the unsaponifiable fat is resin oil or petroleum, shake it with its own volume of acetone. If perfect mixture ensues, the fat is resin oil or a mixture of petroleum with a large excess of resin oil, but if not, the fat is either all petroleum or there is very little resin oil. Alcohol of sp. gr. ·95 can also be used, in which resin oil sinks and petroleum floats. If saponifiable oils are also suspected, we may determine what vegetable oil is present as an adulterant by finding the iodine and saponification values of the original substance, or by ex-

amining the fatty acids set free from the soap, first separated from the unsaponifiable matters, by a mineral acid. This examination may include the determination of the saponification number, temperatures of fusion and solidification, iodine number, etc. The iodine number must be first determined for the free fatty acids, as Hubl's process is only for neutral fats. The author has found for the iodine numbers of the fatty acids the following figures:—

Acids from rape oil	96·3 - 99·02
Acids from earth-nut oil	95·5 - 96·9
Acids from sesamum oil	108·9 - 111·4
Acids from cotton oil	110·9 - 111·4
Acids from linseed oil	155·2 - 155·9
Acids from hemp oil	122·2 - 125·2
Acids from castor oil	86·8 - 88·3
Acids from cocoanut oil	8·39 - 8·49

It is sufficient to act directly on the fatty acids with Hubl's iodine solution. If it is wished to calculate the iodine number J of the saponified fat from the iodine number J_2 of the unsaponifiable fat of the original mixture and the iodine number J_1 of the whole original substance, it can be done by the equation

$$J = (a : 100\, J_1 - b\, J_2).$$

Here a is the percentage of saponifiable fat, and b that of unsaponifiable fat. The first described method is, however, to be preferred, *i.e.* making use of the separated fatty acids, because the same material can be used for the determination of fusion and solidification points, which are very important data in the recognition of fats.

CHAPTER III.

POPPY OIL.

Poppy oil is got by pressure from the seeds of *Papaver somniferum*, specially the black variety, and its production is an important industry in the north of France. About half the oil produced there is used at home, and most of the other half goes to the south of the same country, where it is used for making grain-soap. In Germany poppy oil comes mostly from Baden, Bavaria and Würtemburg. The poppyheads are opened at a certain degree of ripeness, and their contents are shaken out on to sheets of iron, winnowed to get rid of fragments of capsule, and ground to meal in a mill. This meal is put into bags of ticking, and in them into the press. The oil is collected and allowed to settle till clear, when it is sold. The French distinguish two classes: white, for culinary purposes; and red, for technical uses.

Poppy oil is of a pale yellow to a light gold colour, clear, fluid, of pleasant taste, and with a characteristic though feeble smell. It is much used for food, and is sometimes even preferred to olive oil, with which it is used as an adulterant. It does not become rancid easily. The older oils are used as fuel, but give too bad a light to be employed as illuminants.

The second quality, got by hot pressing, has a rough taste and smell.

The specific gravity of the oil is:—

·9285 at 10° C.
·9271 „ 12° „
·925 „ 15° „
·9215 „ 20° „

At 15° C. the oil is 13·6, and at 7·5° C. 18·3 times thicker than water. It freezes with difficulty. It is still clear, though thick, at 15° C., and does not solidify above 20° C. Once frozen to a white mass it does not thaw again till heated to 2° C., when it begins to fuse rapidly.

Poppy oil dissolves in its own volume of ether, and in 25 volumes of cold, 6 of boiling, alcohol. If consists chiefly of linoleine, together with the glycerides of oleic, stearic, palmitic, myristic and lauric acids.

Its ultimate analysis is:—

	Per Cent.
Carbon	78·63
Hydrogen	11·63
Oxygen	11·74

Poppy oil is easily saponified, and gives a hard soap.

CHAPTER IV.

MECHANICAL PURIFICATION OF LINSEED OIL.

Linseed oil is brought upon the market for rapid sale, and contains considerable amounts of such foreign bodies as water and linseed-meal, which, when the oil comes to be used for paints and varnishes, must be removed if a faultless product is to be obtained.

The simplest method of purification requires no plant or outlay, and consists in simply stocking the oil in a receptacle fitted with draw-off cocks at different depths, and leaving it then for weeks or months, or even a year, with free access of air all the time. If the top of the vat must be covered on account of dust, holes should be made in the sides above the surface of the oil.

Where, however, space does not permit of this procedure, mechanical means of purifying the oil must be resorted to. To these means belong:—

1. Machines in which the oil is first stirred up for a long time and then allowed to stand.

2. Machines in which the oil is filtered, either by its own weight or by artificial pressure.

3. Mixing with the oil heavier liquids which when they separate out carry the impurities to the bottom with them.

4. Heating and bubbling hot air through the oil.

These mechanical methods have so far proved themselves superior to chemical means because when drugs are used they have themselves to be got rid of afterwards, and that is always the longest and most troublesome part of the series

of operations. Acids are employed and it is absolutely necessary to get rid of them, as the presence of traces would affect the pigments when the oil was used for paint-mixing. Time has also to be allowed for the oil to clear, and there is a loss by the saponification of part of the oil, which forms a layer which would have to be treated with ether to get the oil from it.

Although in spite of this I shall mention some chemical methods of purification, it is only to make my work complete.

In working on a small scale, it is always best to purify the oil by stocking rather than to use chemicals. On a large scale, one of the machines about to be described is essential, and especially that alluded to in the last of the four categories just mentioned, which allows of rapid and uninterrupted working.

Rieck's Machine.

In the machine of Otto Rieck of Mulheim A is the cylinder fastened in the vessel B and enlarged below. C is a hollow piston, which moves freely, but closely fitting, in A, and has a perforated bottom D is a hollow piston rod attached to the piston and passing through a stuffing box at E into the lower vessel. G is the perforated top of the piston which can be pressed by the screw H down on the filtering material contained in the hollow of the piston. J are weights to enable the pressure of the piston to be regulated, and K is a hand-wheel for raising the piston. M is the cleaning hole, and N a cock.

The apparatus works as follows: The oil to be purified is put into B, and by means of K the piston is lifted. This causes the oil to flow through the valve to the under side of the piston. The piston is then allowed to descend slowly by means of the weights J. This forces the oil upwards through the filtering material. When it arrives above the

piston and flows through a hole in the hollow piston rod into

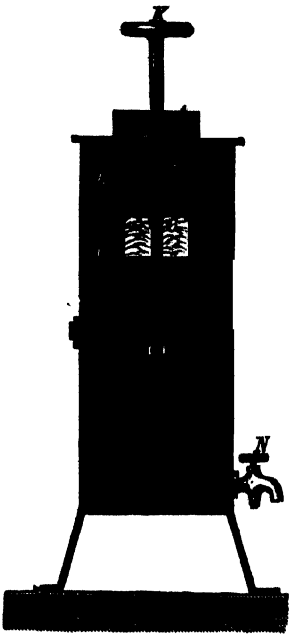


FIG. 1.

the lower receptacle F, the dirt filtered from the oil can be removed through M.

CATARACT MACHINE.

This is made by the Actiengesellschaft für Maschinenbau und Eisenindustrie at Barel in Oldenburg. It is represented in vertical section by fig. 2. The oil to be purified is filled into the cylindrical iron vessel up to a mark. By turning the wheel S, the stirrer Fl is set in rapid motion. The centrifugal force thereby set up in the oil causes it to rise against the sides of the vessel. Thus it is caught by the pro-

jections K and a ring above them, and driven down again through the centre, to be again acted on by Fl. This vigorous stirring brings about an intimate contact between the particles of the oil and the atmospheric air, such as is impossible by any other means or by any other machine. This makes the

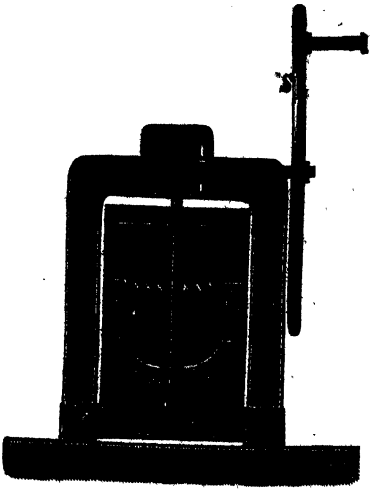


Fig. 2.

machine very suitable for purifying oil, and it can also be used for mixing boiled oil or varnish with pigments.

The Actiengesellschaft makes sizes of the cataract machine holding from 20 to 400 litres. One holding 100 to 125 litres with wheel for hand-driving costs M.250 at Barel. Larger machines are provided with pulleys for belt-driving by power.

Ure's Oil Filter.

Ure has proposed a very practical filter for the mechanical purification of linseed oil. In it the oil is put in a reservoir. This has a tube with a cock near the bottom whereby it can

be put into communication with a cistern of water. The oil filter consists of a cylinder divided into three storeys by perforated plates. The lower storey communicates with the oil reservoir by a short knee-tube. The middle storey contains the filtering material, such as cotton, coarsely powdered charcoal, felt, etc., and the upper storey receives the filtered oil and is provided with a draw-off cock. When the cistern is full of water and the reservoir of oil, the connecting tubes are opened. The water enters the oil reservoir and drives the oil through the filter by hydrostatic pressure. When sediment has accumulated in the lower storey of the filter it is drawn off by a cock. We are thus enabled to separate the clear oil quickly and easily from the sediment & deposits by being purified.

Bags were formerly used for oil filtering, but they soon get clogged. Cotton and loose stuff were tried instead, but these wanted constant changing at a great expense in time and material. When upward filtration was first introduced, the filtering material was almost invariably sawdust. This however has drawbacks which caused its replacement by other materials.

The Upward Oil Filter.

This is packed with linen, tow, moss, or oakum only. The filter-case is of iron lined with lead, and is fed from below through a valve by the hydrostatic pressure of oil from a vessel placed high above the filter. The valve permits of the regulation of the supply of oil to the filter, according to the time available for the filtration.

At the bottom of the filter a cross-piece, H, carries a perforated wooden disc. This is covered with a piece of coarse linen with a finer piece over it. Then comes a thin layer of oakum, E, then one of moss, M, and linen. Then another perforated disc, more oakum and moss, and so on to the top. The screw, S, not only serves for supplying the pressure

which keeps the filtering layers together but by regulating their density decides upon the rapidity with which the oil passes through. The moss used for filtering the oil must have been gathered in a dry season of the year, and must be freed from sand and earth by shaking in a sieve. Moss—*Hyolocomium triquetrum* Schimp; *Hypnum splendens* Hedw; *Polytrichum commune* L.—is a most excellent oil-filtering medium, and can be used without tow or any other adjunct.

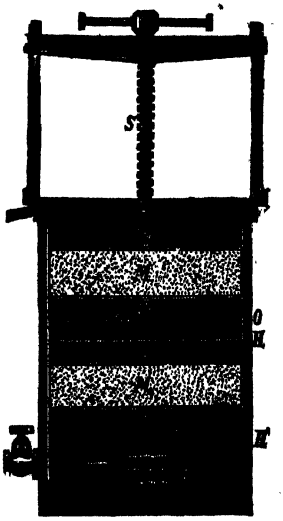


FIG. 3.

If moss alone is used for packing the filter, it must be packed properly by means of the screw S. The moss must naturally be renewed from time to time. If the oil has been stocked for some time before filtering a renewal about every three weeks is sufficient. After a lot of moss has been used for filtration for the last time, hot water and strong pressure are used to get from it the oil which it would otherwise retain.

OIL-REFINING KETTLE.

This new apparatus, shown in fig. 4, is intended for the refining of fresh pressed oils in general and is specially advantageous for use with linseed oil, because the oxygen

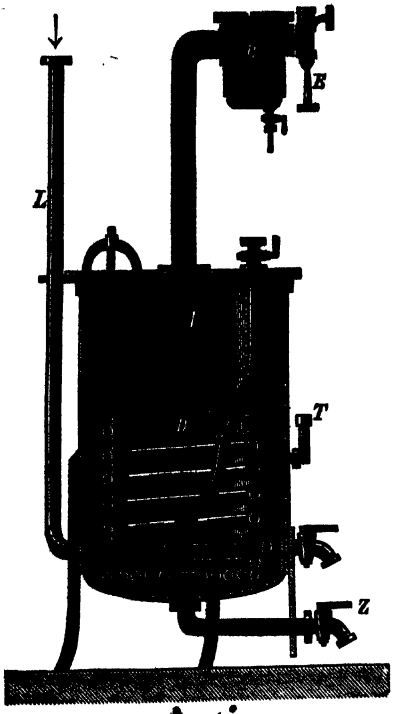


FIG. 4.

action involved in the working of the apparatus makes that oil much more d[illegible]

The boiler or kettle, A, [illegible] about 1½ metre in diameter and contains the steam coil, D, both ends of which pass through the lid. On the lid is a tube carrying the vessel R with an air-ejector, E. When this ejector is set to work, after the

kettle has been two-thirds filled with oil, it causes a vacuum to form over the oil. As this vacuum is produced air forces its way through the oil by means of the tube L. About the same time steam is passed through the coil. Hence the oil is heated, stirred, and brought into intimate contact with atmospheric oxygen all at the same time. The heat removes any water present with the oil, while the oxygen acts upon it chemically.

Oil treated by this apparatus becomes as clear and pure as if it had been through the processes carried out in a regular oil refinery. The apparatus can be used with direct as well as with indirect steam. The precipitates settle quickly and can be drawn off through the cock Z. The water left with the oil can readily be evaporated by setting the ejector to work. A specially interesting feature of this apparatus is that a higher temperature is reached in it than can be obtained with the steam coil. This is due to the friction of the oil particles among one another, just as a rise of temperature is got by shaking a liquid.

CHAPTER V.

CHEMICAL PURIFICATION OF LINSEED OIL.

For purifying linseed oil we use sulphuric and hydrochloric acids, alum, common salt, bichromate of potash, permanganate of potash, etc.

Take for 300-400 kilos. of linseed oil 1 kilo. of fuming sulphuric acid, and add it to the oil in a thin stream and with constant stirring. Then add to the oil a third of its weight of boiling water, stir thoroughly once more, and allow the mass to stand. When the oil has completely risen to the top of the acid water, it is run off and mixed in another vessel with 3 per cent. of dry common salt. The salt removes from the oil the water which makes it turbid and nothing remains but to filter the oil through a bag filled with bran. When these bags are dirty the bran is used for fodder and the bags are cleaned with lime-water or potash lye. The water is not added to the oil in the above process directly after the sulphuric acid, but after the oil and acid have remained together overnight. This enables the sediment to settle well and to consolidate at the bottom, so that the oil can easily be drawn off clear. One should then dissolve for every 100 kilos. of oil 250 grammes of common salt in 10 litres of water, and pour the solution as hot as possible into the decanted oil, and stir for one or two hours, or as long as is necessary to form a delicate white froth on the oil. The appearance of this froth is a good sign, but it is also an indication that the stirring must be stopped, or the oil will become dirty and

thick and never get clear. If we now leave the oil for about two days in a fairly warm place it separates perfectly bright and clear. It is then filtered either through well-washed and perfectly dry river sand or through felt hats with wide crowns.

According to Evrard, oil is purified by shaking it up with a dilute solution of caustic potash or soda, drawing off the unsaponified oil which rises to the top, and shaking it with water, and again allowing it to separate. Wagner considers that zinc chloride may be substituted for sulphuric acid with advantage. It is said to dissolve the mucilaginous bodies, and in time to carbonise them, without affecting the oil. A syrupy solution of chloride of zinc is shaken up with fifteen times as much oil. The oil becomes turbid, but by treatment with steam or warm water after standing again clears. Tilchmann recommends sulphurous acid for purifying oil. He passes the gas in a stream through the oil heated to 260° C (?)[1] for four hours, and then drives off the acid present by means of steam. The effect can be produced at lower temperatures, but takes longer. Probably the sulphurous acid becomes sulphuric in the linseed oil, and forms sulpho-fatty acids. Another, and very excellent method, is to use permanganate. The process is not only decidedly quick, but partially bleaches the oil, which is an additional advantage. The salt not only bleaches but destroys fragments of cellular tissue, etc., and hence its purifying action. To purify 100 kilos. of linseed oil we prepare a solution of one kilo. of crystallised permanganate in 30 kilos. of distilled water at the ordinary temperature, and stir the solution into the oil. Keep the mass stirred for two hours, and then leave it to stand. The oil separates completely from the permanganate solution in the course of a day or two, and can then be drawn off, paler in colour than before, and free from all impurity.

[1] The query is Andés's.

COMBRET'S APPARATUS.

The apparatus of Raymond Combret enables us to combine mechanical with chemical purification. In it thin streams of oil are purified by passing through various solutions of salts. The process is carried out in the cylinders B (figs. 5 and 6), of which several are used, to permit of continuous working.

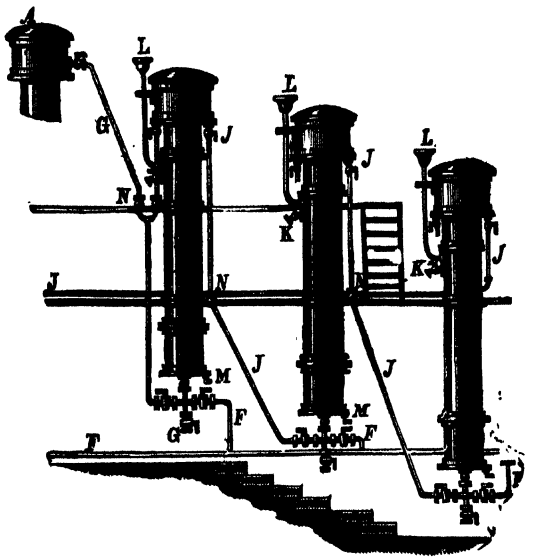


FIG. 5.

The oil is placed in the reservoir A and goes through a pipe C and rose D into the tinned iron cylinder B, which opens above into another cylinder of larger diameter closed by a lid. The cylinders contain water or solutions of chemicals.

The tube C brings the oil to a T shaped tube, E, connected with the steam pipe F for heating the solutions in the

cylinders. The tube leading downwards with the cock G serves to clean out the tube E. The rose distributes the oil through the contents of the cylinder, which rises through the liquid to float on the surface in the wide upper part of the cylinder. Thence the oil can be drawn off by the cock H, while the cock J leads the oil to the next cylinder or to the filter. The surface of the liquid in the cylinders can be brought accurately to the height of the cocks H and J by drawing it off through the cock K or by adding more through the tube L. The cylinder is emptied by means of M. The battery of cylinders must be so arranged that the bottom of the wide upper part of the first is above the whole of the second, and that the same relationship subsists between the second and the third, and so on, so that the oil may flow through the battery by its own weight. It is led by a pipe after leaving the last cylinder into the filtering apparatus. It is a very good plan to insert a small rotatory pump N in the tubes J and C, so as to increase the velocity of the oil as it enters the cylinder, and if necessary to drive the purified oil through a tube O, fixed to the cock D, back to the bottom of the same cylinder.

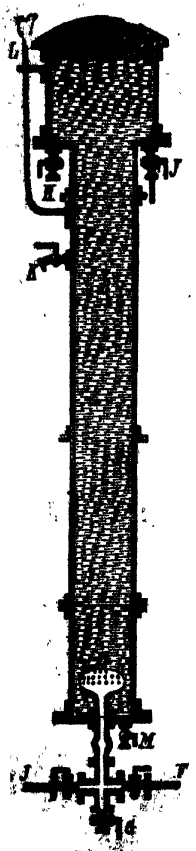


FIG. 6.

By this process we are enabled to use the various chemicals applicable to the purification of oil, such as sulphuric acid,

chromic acid, manganic acid, sulphides, etc., according to the effect they are to produce.

For certain purposes, *e.g.*, in the preparation of extra pale oils for white pigments, the foregoing processes are insufficient, and bleaching must be resorted to in addition to them, as they affect the yellow colour of the oil only imperfectly or not at all.

CHAPTER VI.

BLEACHING LINSEED OIL.

BLEACHING may be natural or artificial, that is to say it may be done by the action of the sun or with chemicals, and the natural method is distinguished by its name from the more rapid process of chemical bleaching.

SUN BLEACHING.

Schädler says in his *Technologie des Oele und Fette*, speaking of bleaching and the action of various bleaching agents: "The usual chemical action of light is to separate oxygen from various bodies, for light promotes the combination of atmospheric oxygen with the hydrogen and carbon of the organic substance of the dyes, whereby the latter are usually destroyed or changed into lighter shades. In many cases the special action of light may depend on its promoting the formation of ozone or peroxide of hydrogen, which when formed oxidise the colouring matters more easily than the oxygen of the air. The most powerful bleaching action is naturally exerted by the light of the sun. For chemical bleaching many various things are used, but all may be reduced to the action of ozone, peroxide of hydrogen, chlorine, and sulphurous acid. The first two act by oxidation. Chlorine removes hydrogen, forming hydrochloric acid and replaces it by itself. Sulphurous acid forms a colourless compound with the colouring matter."

To carry out oil-bleaching by the sun on a large scale, we use wooden vats lined with zinc, or make the vessels entirely

of lead. In the latter case, the increased durability of the receptacles under constant use well repays the extra initial cost. These vessels are best made one metre long by half that width, and 15 to 20 cm. deep. They must be provided with well-fitting lids, so as to protect the oil from rain. The lid has a large pane of glass in it, and is slightly slanted for rain to run off it easily by having one of the sides of the vessel 2 to 3 cm. higher than the other. It is also of importance that air should have free access to the oil. Hence two tubes open at both ends are put through the sides of the vessel, opposite each other, so that a constant current of fresh air is supplied to the oil. In the course of a fortnight the oil in the vessels will become quite white and clear, and only requires to be drawn off. The sediment can be added to common oil for boiling. To accelerate the operation chemicals may be added to the oil. For example, a small addition of 96 per cent. spirit is of great advantage, and the action soon becomes noticeable. Linseed oil is almost always mixed with ferrous sulphate, peroxide of manganese, or hydrochloric acid, to hasten the bleaching.

Rapid bleaching can also be effected in rooms of which the atmosphere is kept full of ozone by electrical apparatus, or by keeping sticks of damp phosphorus about.

Peroxide Bleaching.

Peroxide of hydrogen, which is now made on a large scale in many chemical factories, and put on the market in the form of a 10 per cent. solution, is a good medium for oil bleaching, as it only requires to be well shaken up with the oil, and bleaches it in a few days. The bleached oil also separates very readily and completely from the peroxide solution and can easily be drawn off. For linseed oil 5 per cent. of its weight of 10 per cent. peroxide is enough. Bleaching with permanganate, manganate or bichromate of

potash depends upon the action of ozone. The bleaching is done in large wooden vessels lined with lead, and provided with a stirrer and a heating coil. A solution of permanganate or bichromate made strongly acid with sulphuric acid is gradually stirred in, and the stirring is then continued for thirty to sixty minutes longer, unless the bleaching is finished sooner. Then after standing six to twelve hours the oils will have risen clear above the green chrome alum-containing or brown manganese alum-containing solution. The acid liquid is run off and the oil is washed two or three times with warm water and left to stand. The clear oil is then ladled off. Between the clear oil and the water, a layer of emulsion will be found. This is best treated with 10 to 15 per cent. of petroleum-ether, which at once separates the oil in it from the water. The ether is recovered by distillation after enough of it has been collected from several bleaching operations, and is used over again for the same purpose. One hundred kilos. of linseed oil require from 500 to 600 grammes of bichromate or permanganate, together with twice the quantity of sulphuric acid. The acid is diluted with five to six times its bulk of water before use.

Sulphuric Acid Bleaching.

For bleaching with sulphuric acid, we take a litre of the acid for 100 kilos. of oil, first diluted with 30 litres of water. The whole mixture having been warmed up by the steam coil is additioned gradually with very finely powdered peroxide of manganese, till the at first brown mass has nearly turned white. At the close, the oil is washed, and then treated as before directed.

Sulphurous Acid Bleaching.

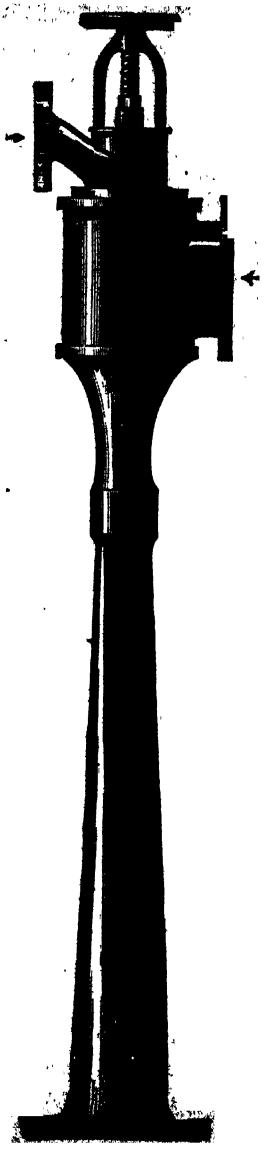
As all fats, even linseed oil, are much attacked in bleaching by chlorine, I consider the method quite inapplicable, and

we use the cheap acid sodium bisulphite, a concentrated solution of which shaken up with the oil is of great service. But to bring all the sulphurous acid present into play we also add dilute sulphuric acid. This is done on a large scale in vats lined with lead. For a metric hundredweight [1] of linseed oil from 1 to 1½ kilo. of the bisulphite is required. The sulphuric acid must be added in excess, but very gradually. If the acid is put in too quickly the sulphurous acid is evolved so rapidly that it escapes without doing any work.

According to Schädler, Körting's aspirator or a steam aspirator is very suitable for use in bleaching with sulphurous acid.

The steam apparatus (fig. 7) is made of hard lead. The high pressure steam enters it as shown by the arrow, and passes inside through a number of hollow cones. This sucks in the air at high velocity and drives it out from another opening.

This apparatus can be used to produce either suction or pressure, *i.e.*, to rarefy or compress air, according to require-



ment. It is so constructed that with a steam pressure of three atmospheres it will control by suction a water column of 3 to 8 metres and one of 3 to 4 metres by pressure.

In fig. 8 an air aspirator is shown fixed to the top of a vat

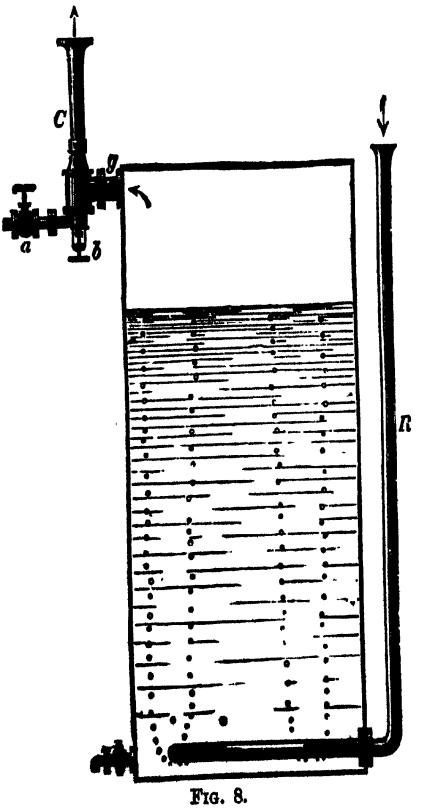


FIG. 8.

containing the oil to be bleached. It sucks, through the pipe and a perforated coil, sulphurous acid, which passes through the oil in an extremely finely divided state, till the bleaching is perfect. The vat must of course be closed and

ir-tight. The sulphurous acid is generated in a very simply uilt stove by burning sulphur in a draught of air, also pro-uced by the aspirator which draws the gas into the oil. A team valve is provided to regulate the rate at which the gas asses through the vat. The apparatus works very reliably ndeed, and can be used even with viscid oils. The oil is nally rinsed from the acid by the methods already described.

CHAPTER VII.

OXIDISING AGENTS FOR BOILED OIL MAKING.

According to the principle established by Mulder, that to give linseed oil good drying properties it must be acted upon by oxygen at a high temperature, oxidising agents play no small part in the manufacture of boiled oil. How long we remained in ignorance as to the nature of the substances to be used is sufficiently shown by the fact that both text-books and old oil-boilers recommend the use of such driers as fish bones, whiting, onions, garlic, verdigris, lime, tin, lead, alum, ferrous hydrate, etc. All these substances are utterly useless, and the progress of chemistry has taught us that the following are the agents which can be employed with success in making boiled oil: atmospheric oxygen, red lead, litharge, suboxide of lead, sugar of lead, manganous borate, acetate and oxalate and the linoleates of lead and manganese.

I can pass over these substances as they are already well known, and will only mention that very lately attempts have been made to abandon the oxidation of linseed oil by heating in it certain compounds of lead or manganese which decompose at a particular temperature, and to use nothing but oxygen or ozone. The reason of this change of front is that the metallic driers always darken the oil more or less, which is for many purposes a very great drawback. In a subsequent part of this work several proposals of this nature will be exhaustively discussed. Here I will content myself with describing some new linoleate driers.

Among the many drawbacks involved in the use of the

ordinary chemicals employed in making boiled oil, such as litharge, lead acetate, red lead, peroxide of manganese, manganous borate or hydrate, etc., one is that they never decompose completely. Hence quantities of them are wasted. Again, the boiled oil made with them is hard to clarify. They remain long suspended in the oil. These evils have instigated a search for new driers, among which the linoleates deserve special mention.

But before I discuss these new driers fully, I will make some remarks on linoleic acid, which is the chief constituent of linseed oil, from Schädler's much-quoted work.

Linoleic acid (C_{16} H_{27} HO), or according to K. Peter's C_{18} H_{32} O, is called linolein by Mulder. It and its salts are little known, on account of their instability. To make it, linseed or poppy oil is completely saponified with caustic soda lye, and the soap is purified by repeated relarging. The soap is dissolved in an excess of water and precipitated by calcium chloride. The lime salts of the fatty acids thus thrown down are washed with water, drained, pressed to get rid of most of the water, and treated with ether. This dissolves only the linoleate, thus separating it from the other lime salts. The ethereal solution is mixed with cold dilute hydrochloric acid, when linoleic acid is set free and remains dissolved in the ether floating on the watery liquid.

The solution of linoleic acid in ether is decanted, and the ether is distilled off in a stream of hydrogen at the lowest possible temperature. The residue is dark yellow and is impure linoleic acid. It is dissolved in alcohol and precipitated as barium linoleate with chloride of barium and ammonia. The precipitate is washed, drained, pressed, dissolved in ether, and crystallised from ether several times. The pure crystals of barium linoleate are then shaken up with ether and dilute hydrochloric acid and the ethereal solution of linoleic acid is distilled in hydrogen as above described. The linoleic acid, which does not distil off, is

dried in a desiccator over sulphuric acid and a mixture of lime and ferrous sulphate. The sulphate is to absorb oxygen, and prevent oxidation of the linoleic acid. A nearly pure linoleic acid is got by decomposing lead linoleate with sulphuretted hydrogen, and dissolving the linoleic acid from the lead sulphide with ether.

Linoleic acid is a thin, pale yellow oil, of ·9206 sp. gr. at 15° C., with a high refractive index, and a weak acid reaction. It has a mild taste, followed by a rough after-taste. It is still liquid at – 18° C. It is insoluble in water, but freely soluble in alcohol or ether. On exposure to the air it greedily absorbs oxygen to the extent of about 2 per cent. of its weight, thereby becoming tough and thick like a varnish. Thin layers of it dry on wood in the air, but on glass never become quite dry. Linoleic acid is not volatile without decomposition and on distillation gives different products from oleic acid. No sebacic acid is then formed. Nitrous acid thickens linoleic acid, but causes no separation of crystals of elaidic or any related acid. Nitric acid forms a slimy resinous mass with much frothing.

New Driers—Linoleates.

It is difficult to produce pure linoleates, because they readily decompose, forming acid salts. They are white, for the most part uncrystallisable, and separate out in flakes on cooling from solution in hot alcohol or ether. By spontaneous evaporation a jelly is left. These salts turn brown in the air and acquire a characteristic odour.

Manganous linoleate is sold by Dr. J. Wilhelmi of Reudnitz-Leipzig in the form of a pale brown solid. This is really a solid manganese soap, and serves for the preparation of all manner of liquid siccatives. According to Wilhelmi's directions for the preparation of a well-drying boiled oil 100 lb. of raw linseed oil are kept at about 150° C. for five hours, with

1 lb. of the manganous linoleate, previously dissolved in a little linseed oil. When cold, the mass, if painted thin on glass, dries quite hard within twenty-four hours. The doctor's factory also supplies a liquid drier, which will at once produce a clear pale yellow oil.

Dr. Wilhelmi is said to have discovered that the formation of boiled oil is not (?)[1] due to oxidation, but to a solution of the manganese in the oil, and for this reason adds a solid compound of linseed oil with manganese to the boiling raw oil, using the manganese compound as a carrier of oxygen.

Another new sort of drier for making boiled oil quickly has been lately made by Dr. Höhn & Co. of Dusseldorf in the form of

SOLUBLE MANGANESE AND LEAD PREPARATIONS,

two sorts of the former and one of the latter.

The manganese preparation No. 1 is the richer in manganese and therefore the more active of the two. It is, however, darker than No. 2, which has no influence on the colour of the linseed oil. The manganese preparations have distinct advantages over the usual insoluble ones at present on the market. By virtue of their solubility their high percentage of manganese is made fully available, the manganese is completely taken up by the oil and dissolved clear, so that even small quantities of the drier give well-drying oils which remain clear, and require no keeping in stock.

As the preparations make quite clear solutions, any required proportion of manganese can be added to the oil, while in using insoluble or only partially soluble preparations of manganese we must always remain in doubt whether the oil has taken up exactly the desired amount of manganese. The preparations dissolved at low temperatures, and mere fractions of the quantities of manganese hitherto required are sufficient to make the oil fully drying.

[1] The query is Andés's.

To get a good drying oil we proceed as follows: The linseed oil is heated to 120° to 140° C., and then 1 per cent. of manganese preparation No. 1, or ½ to 2 per cent. of manganese preparation No. 2, is added with constant stirring. The oil froths at first, but this soon ceases, and when it does the oil is ready. If the lead preparation is also used, we take 1 per cent. of it together with ½ to ¼ per cent. of manganese preparation No. 1, or ½ to ¾ per cent. of manganese preparation No. 2. The result dries well and gives a specially hard coat.

If I make some more remarks here on the method of adding driers, I do so in order to combat erroneous notions.

Formerly it was believed that the drier ought not to come into contact with the oil, so that it was hung in the oil in linen bags, often in an unpowdered state. As, however, the oxidising substance was exposed to the oil in a compact mass, it was impossible to oxidise the oil properly. The parts of the substance nearest the sides of the bag certainly parted with their oxygen, but the inside of the mass remained unchanged, so that the oil got too little oxygen, and the result was naturally very inferior. The oxidising chemicals added to the oil cannot act powerfully unless offering the greatest possible surface to it, *i.e.*, unless in the finest possible powder, so that every particle of it comes into contact with the hot oil. If these preparations are added to the hot oil, the evolution of oxygen is visible, and extraordinarily rapid and energetic. The oil froths tremendously and will easily boil over if care is not taken. Trials with large quantities of oil have convinced me that driers had a greater effect on the drying qualities of the oil when added to the hot oil than if put into the cold oil and heated up with it. It is of course necessary to add them to the hot oil a little at a time, or else the pan boils over, with great waste of oil and danger of fire.

The quantities of single driers which are required to make

a good boiled oil depend, firstly, on the nature of the oil, and, secondly, upon the amount of drying power required. In general, we require less of a manganese preparation than of a lead one, which is less energetic. The usual amounts necessary are:—

	Per cent.
Manganese preparations	1-1½
Lead preparations	3-5

they being kept with the oil at a boiling temperature for three hours; then we shall get an oil drying within thirty-six hours. For quicker drying, larger proportions must be taken than those just given, and the percentages may rise for manganese preparations to 2 to 3 per cent., for lead preparations to 5 to 8 per cent., and the boiling time to 5 to 8 hours. A further increase of the quantity of drier is impracticable, as larger amounts would partially saponify the oil. If other preparations, *e.g.*, peroxide of manganese, are used, the above percentages must be increased in order to make up for the diminished amount of manganese in the drier.

CHAPTER VIII.

THEORY OF OIL-BOILING.

THE Dutch chemist Mulder was the first to occupy himself seriously with the drying oils, and the changes they undergo on drying and boiling, and we have to thank him for some knowledge of the theory of the preparation of boiled oil.

Linoleic acid forms about 80 per cent. of linseed oil, as already stated. When a great surface of it is exposed to the atmosphere it readily becomes oxidised to linoxic acid, a change which is rapid or slow in proportion to the freedom or the reverse with which air has access to the oil. The oxidation is accelerated if the oil is heated while in contact with oxygen, and we may proceed in three ways, acting on the oil with pure oxygen, or with air from which the oil absorbs that gas, or with metallic oxides or other compounds rich in oxygen. The oxidised linoleic acid thus obtained is the chief cause of the drying properties of all boiled linseed oils. If linseed oil is boiled by itself in a wide shallow vessel, it becomes better drying than before by taking up oxygen, and if linseed oil is exposed for a long time to the air without being heated its drying properties are again somewhat increased, but never to the same extent as with boiling. It follows that to get drying linseed oil a high temperature is required, and at the same time the action of oxygen in some form.

Boiling linseed oil sets free more or less of its glycerine, and time and light and oxygen have a similar action. It is clear that boiling must begin, promote, and finally complete the separation, leaving behind more or less free linoleic acid.

Every drying oil has its drying power increased by boiling, and it would appear that such is the more the case the longer the boiling has been kept up.

In this boiling three different processes are involved: 1. All the anhydride of linoleic acid present in boiled oil does not need to dry, it is dry, elastic, and can dry no more. 2. All the free linoleic acid still present turns later to linoxic acid, which dries very slowly. 3. All the unchanged linoleine still present dries later to linoxine. The anhydrite gives an elastic india-rubber-like coat, the second resembles turpentine, and the third coat is like leather.

Boiled linseed oil then in the main is more or less decomposed linoleine, containing the anhydride of linoleic acid, while glycerine is still combined in the undecomposed part of the linoleine. In proportion to the duration of the boil there will be more or less oleine, palmitine and myristine present.

In making boiled oil for ordinary painting we have first in view the necessity of obtaining a product which will dry as quickly and as hard as possible. This result is obtained, not when the boiling oil is acted on with air or oxygen, but with oxidising compounds. By oxidation of the linoleic acid to linoxyn, and by compounds of linoleic acid the oil becomes rapidly hard drying, and if we boil linseed oil with red lead, sugar of lead, or litharge we get more or less linoleate of lead formed, and linoleate of manganese if we boil it with compounds of manganese. If we examine these salts, we find that linoleate of lead is a hard pulverisable substance, while manganese linoleate is tough and elastic. These circumstances have to be noted by any one who wishes his boiled oil to answer the purpose for which it is intended.

The researches of Mulder have shown that the formation of boiled oil proceeds—

1. From the setting free of a part of the linoleic acid and other fatty acids of the linseed oil.

2. From the formation of salts of the fatty acids by the bases of the driers.

3. From the formation, or the creation of the possibility of the formation, of anhydride of linoleic acid.

4. From the co-operation of two or. more of the above. Every drying oil will give, without special treatment, the leathery linoxyn and free fatty acid, which are more quickly formed by boiling the oil.

CHAPTER IX.

MANUFACTURE OF BOILED OIL.

THE theory of this and a description of the various driers have already been given, and I can therefore now proceed to a minute description of the processes.

BOILING OVER THE OPEN FIRE OR WITH STEAM.

Boiled oil can be made from ordinary mercantile oil, after the usual lying by, by boiling in iron or copper pans over an open fire or by means of steam. Care should be taken that the form of the pan is such that the oil offers as much surface as possible to the air. Otherwise the shape is immaterial. The size of the boiling vessels depends on the scale in which the manufacture is carried out, and all sorts and sizes are in use, from those of a capacity of 50 kilos. only to those holding 1,000 kilos. Small vessels are usually so arranged that they can easily be lifted off the fire, while the larger ones are bricked-in and provided with special safeguards against accidental fire, or the boiling over of the oil. Among the safeguards against fire may be mentioned heavy iron lids, which are slung to the roof of the boiling house and are lowered from above, so as to close the mouths of the vessels if a conflagration is started and put out the flames by excluding the air. Another plan is to provide means whereby the oil can be run off from the bottom of the pan to a cold receptacle at some distance. The arrangements directed against a boiling over of the oil, and especially against any that may boil over finding its way into the

fire, consist in a gutter surrounding the mouth of the pan, which catches the oil that overflows, and from which the overflow is led away by a pipe. Another way is to have the pan so large that there is no necessity to fill more than two-thirds with oil, and to brick it in so that the fire has no access to the empty part of the kettle, and that no oil which boils over can get into the fire. The pan can also be provided with a head from which a pipe leads the vapours into a chimney, where a small fire is maintained in order to burn them.

The highest temperature which should be used in making boiled oil by means of the driers, specially mentioned above, is 230° to 250° C. A heat above this makes the oil too dark in colour. According to my latest experience, I recommend the following boiling method for all boiled linseed oil, whatever driers may be being boiled with them. The linseed oil is heated, at first slowly, then more quickly, until it begins to froth. It is then quickly brought to the maximum temperature, at which its original golden yellow colour turns to a pale greenish yellow. Either the kettle is now lifted off the fire, or the fire is drawn, and the oil is allowed to cool to 130° to 150° C. At this temperature the desired driers are added in proper quantities, a little at a time. The boiling is then resumed until the oil is ready, and has the proper drying power. Care must be taken to keep the temperature between the limits, neither below 230° nor above 250°. This process gives pale boiled oil under all circumstances, while the ordinary method usually darkens the oil by the time it is ready.

However the boiling has been conducted the oil must be left to stand at the conclusion of the operation, in order that the organic matter carbonised by the boiling and any undissolved driers may separate out, and settle to the bottom. As long as the oil is hot it is thin, and the specifically heavier bodies suspended in it, whatever may

be their state of subdivision, will separate from it then much more readily than when it thickens on cooling. The sediment consists of original impurities as well as substances added during or formed by the boiling, and the amount of it is naturally various for those reasons. It averages however from 5 to 8 per cent. Its colour depends on the quality of oil used and may be white, yellowish, dark green or even black. According to my experience, white or yellow sediment is a mark of an inferior oil having been used. The sediment from a good oil is dark coloured, and should show no granular or crystalline structure. The drying power of the sediment, which constitutes the only loss if the oil has not been heated above 220° C., is very great indeed, on account of its richness in driers, so that it is used for numerous purposes.

It is specially advantageous to substitute steam for a naked fire in the preparation of boiled oil, and if the use of steam for this purpose is not yet so common as it ought to be, the reason is that it does not pay to provide steam for this purpose alone. There must be a steam-engine, and hence the method is only practicable in places where much capital is or can be sunk in plant. Steam-boiling of oil is mostly practised in jacketed pans, but occasionally by means of a steam coil. The latter has the disadvantage as compared with the former arrangement that it is very difficult with it to get a high enough temperature. According to the construction of the apparatus the steam is or is not superheated. In the latter case its use is attended with difficulties and dangers, but most oil-boiling factories are nowadays worked with superheated steam, so much has the management of it improved of late years.

One of the most simple plants consists of a pan, wider than it is deep, and made of strong boiler-plate, and which has been tested to a pressure of from four and a half to five atmospheres, and has a double bottom. The pan is provided

with a safety valve, an inlet and an outlet pipe for steam, and a pipe for running off condensed steam from the jacket. The pan is filled with oil and steam is passed through the jacket at a steady pressure of four and a half to five atmospheres. An improved form of this apparatus has a steam coil in the oil, as well as a jacket, and also a mechanical stirrer, so as to increase the surface which the oil exposes to the air.

Another plan is to superheat steam by means of an ordinary superheater or system of piping, and then to blow it direct through the oil to be boiled. The temperature of the steam must of course be known and be carefully regulated.

Zwieger's Process.

H. Zwieger of Zwickau has patented in Austria Hungary (No. 1,768) a process for making boiled oil and oil varnishes, in which the steam proceeding from the fusion apparatus at about 350° C. is used for boiling.

Lehmann's Superheater.

The process of Holzwich and Zimmermann (D.R.P. 9,444), which shall be specially mentioned later on in this section, has lately been improved by R. Lehmann of Dresden. Lehmann uses steam superheaters of the following construction. In contrast to most or perhaps all the older types, consisting either of sets of tubes connected by elbows or stuffing boxes, or coils welded together into a single piece, Lehmann uses in his improved superheater elastic joints so that the superheater can expand in the fire without risk of becoming cracked or leaky at the joints. Each tube is double, *i.e.*, consists of two co-axial tubes. The inner tube opens near one end of the outer, which is closed. The steam flows from one inner tube into the tube surrounding it, from that into the next inner tube, then into the tube surrounding that,

and so on. This increases the exposure of the steam in the superheater to twice the usual amount without increasing

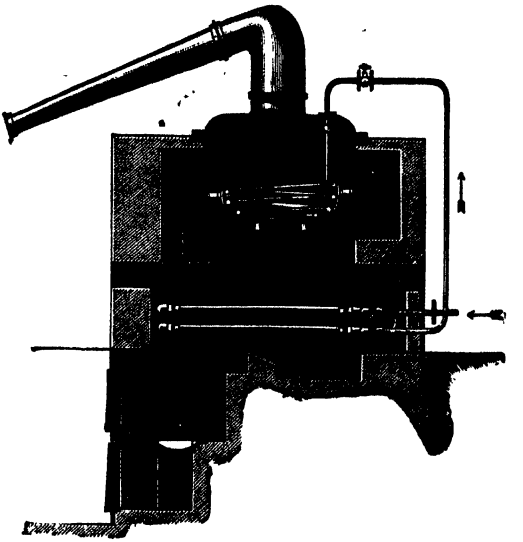


FIG. 9A.

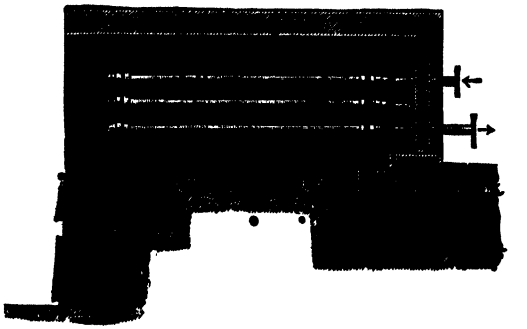


FIG. 9B.

the number of tubes or the space occupied by the apparatus. In other words, this superheater combines great heating

surface with economy of space, and hence of fuel, while at the same time that the construction secures those advantages. it improves the superheating effect, and makes the substitution of fresh parts in case of accidents very easy.

Fig. 9 shows Lehmann's superheater arranged below the boiling kettle, so that the gases which have heated the superheater can help to heat the oil before they finally pass into the chimney.

Andres' Process.

According to Andres, it is unnecessary in boiled-oil making to use steam, as hot air will do as well. If his method is to be adopted a fan is used to drive a stream of air through a superheater, then through the oil, and thence back to the fan, and so round and round, always working with the same lot of air.

Walton's Process.

According to an English patent by F. Walton, the inventor of linoleum, a process for boiling oil consists in heating the linseed oil in wide open pans by steam. It is then raised into a chamber heated by steam, where it is beaten by paddle wheels. Being thus scattered through the air in drops, it offers a very large surface for the absorption of oxygen. The chamber may have glass windows so that the light of the sun may co-operate in producing the effect. The oil finally collects in a gutter on the floor of the chamber, whence it can be returned to the pans if more heating is still required.

Vincent's Process.

Vincent's apparatus for boiling oil by steam is a pan, preferably of copper, with a circular transverse section. Its depth is about the same as its diameter, and its bottom is convex. Up to its middle the pan is surrounded by a strong iron jacket for the admission of steam. Both pan and jacket

must be capable of standing a pressure of eight atmospheres. The mouth of the pan is closed by a head provided with a manhole. Through a stuffing box in the middle of the head passes a vertical hollow cylinder with a solid one inside it. These rotate in opposite directions, and operate the stirrers which work up the oil. The combustible vapours escaping from the hot oil are led beneath the pan to economise fuel.

The oil to be boiled, which is first stocked for some time in large vats, is heated to about 35° C., and then pumped into the pan. Full steam is then turned into the jacket, and the stirrer is set in motion. When the pressure has risen to two to three atmospheres, air is admitted. The oil immediately froths and swells up greatly, and the mass previously a dark brown becomes a pale yellow. If a darker oil is wanted the driers—the choice of which is generally regarded as a secret—are rubbed up with oil and poured into the pan in a thin stream through a funnel. The proportion is 375 grammes of driers to every 50 kilos. of oil. When the driers have been added, nothing more has to be done but to see that the steam pressure does not sink below six atmospheres. It is best to keep it at seven atmospheres, so that the air pump which drives the air through the oil, and also the stirrers, may not stop. Vincent has not ascertained how much air is necessary to oxidise any given quantity of oil. Some oils, as a matter of fact, require more air than others, but the usual course is to drive in as much as the oil will take up without priming and coming over into the tube which leads away the vapours caused by the heating. After treatment for about four hours the oil can be run out of the pan into a vat in which it is allowed to stand until it has completely deposited all sediment.

Schrader and Dumeke's Process.

Drs. Schrader and Dumeke have made numerous researches, as a result of which they have discovered that

ozone, after a brief contact with raw linseed oil, not only converts it into "boiled oil," but bleaches it at the same time. The ozonised oil is completely bleached by a single day's exposure to light and air in shallow vessels. The "boiled oil" thus prepared from raw unbleached linseed oil is said to be as colourless as water, to dry quickly, and to be made without heat and with perfect safety, and without any loss or waste. The ozone is aspirated or forced through the oil in suitable vessels, and can be prepared by any of the known processes.

Müthel and Lütke's Process.

The patent of Müthel and Lütke (D.R.P. 29,961) protects the manufacture of boiled oil by treating the raw oil with various gases, which will give nascent oxygen on electrolysis. Such mixtures are chlorine and steam, sulphurous and nitrous acids, nitrogen, oxygen and steam and nitrous oxide and air. One of these mixtures is exposed in the apparatus shown in fig. 10 to a long and powerful silent dark electrical discharge, whereby a high degree of oxidation is given to the oil, if the quantity of gas is sufficient. It is impossible to give an exact chemical formula of the product formed, as it depends on the gaseous mixture used, and on the proportions of its ingredients. Thus if chlorine and steam are used we get hydrochloric acid and oxygen, and with oxygen and sulphurous acid they must be present in such proportions that the electrical discharge can produce SO. It appears to be advantageous, as giving the highest oxidation, to have the oxygen-compound in the gaseous mixture in excess. The apparatus used by the inventors to prepare the oxidised gases consists of a series of so-called condensers, in which the gases are exposed to the electrical action for a very long time, see figs. 10 and 11.

The electricity is produced by a dynamo, into the circuit

of which the primary coil of the induction apparatus is inserted. The secondary coil is connected up with the condensers, which are arranged according to the E.M.F. required. Fig. 10 shows the complete plant. From the steam boiler A a main pipe takes to the cylinder of the steam engine; from *a* two branches, *b* and *c* proceed. Steam is carried by *b* to the coil S in the container B, to heat the

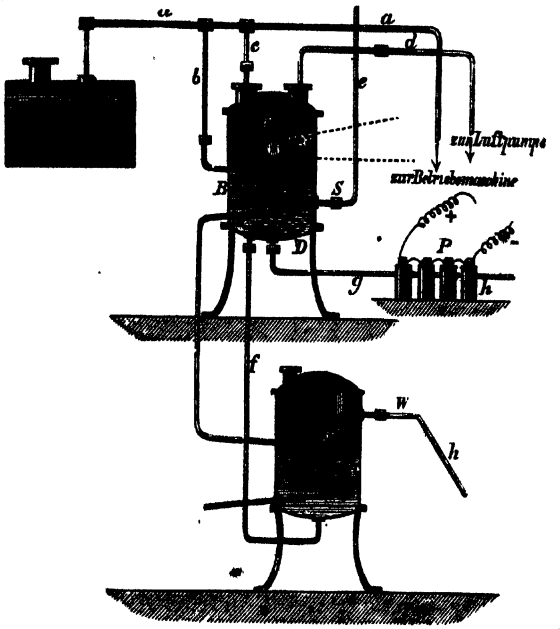


FIG. 10.

oil therein which is admitted by the pipe *c*. At the bottom of B is a flattened coil D, full of perforations, and which is continued to form the tube *g*. This tube communicates with the oxidation apparatus P, to which the gas to be oxidised is brought by the pipe *h*. Fig. 11 represents an

oxidation apparatus in detail. It is made of glass and consists of two tubes, A and B, one inside the other. The two are fixed together by *x x*. A is closed below and is enclosed in an iron vessel C, and rests on the somewhat projecting rim of the latter. The axis of B is occupied by a tube E, which opens into the space between A and B and brings in the gas to be oxidised. The gas then passes out through D into another oxidiser, and so through the entire battery. The parts shaded in the figure are filled with any good con-

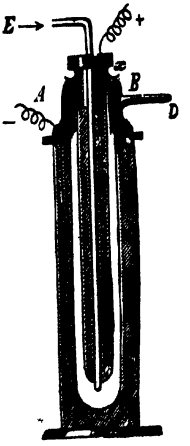


FIG. 11.

ducting material, and connected with the dynamo by the wires + and − . In fig. 11 the apparatus is represented diagrammatically only. The boiler B contains one or more paddle wheels C, on an axle passing through a stuffing box at *x*.

The practical carrying out of the process is as follows: When the apparatus is set to work B is half filled with the linseed oil to be oxidised, by means of *c*; *e* is then shut, and the oil is heated by means of the steam coil to from 60° to 80° C. The vessel B is then connected up, by means of *d*,

with the air-pump, which will give a 73 mm. vacuum. The oxidation apparatus is next put into the dynamo-circuit, while a mixture of sulphurous acid (SO_2) with oxygen and air in equal volumes is passing through it. At the same time *g* is opened, so that the gas oxidised in P is driven through the linseed oil in fine streams, these being a partial vacuum above the oil. All the time the gas is passing the paddle wheel is at work, making the oil expose as much surface to the gas as possible by energetically stirring it up. This greatly accelerates the decomposition of the compounds of the fatty acids, and in a correspondingly short time we get a pale thinly flowing product, which readily dries in the air to a tough and solid mass. The same success attends the use of a mixture of nitrous oxide (N_2O) with three-quarters of its volume of atmospheric air, or of nitrous oxide alone.

The use of the other gaseous mixtures above mentioned may also be resorted to, and the patentees keep them before them, as it is a question of producing from any suitable materials, and by means of the silent electrical discharge, either nascent oxygen or highly oxidising compounds of oxygen, the latter being decomposed by contact with the hot oil. The products of decomposition pass away through the air pump together with a little unused gaseous mixture, and the whole can either be regenerated or used to help the firing of the steam boiler. When the oxidation is finished, a point which is ascertained by taking samples from time to time, the pipe is closed, the stirrer is stopped, and a short time afterwards the pipe *d* is closed and E is opened. Steam now enters the vacuum, and drives the boiled oil through *f*, which is opened for the purpose, into the apparatus, W, which is itself full of very dilute ammonia, and is heated by the coil S' which is fed by the exhaust from S. The oil passes up through this ammoniacal water, which frees it from any adhering acid. It then passes direct through *h*

into the stock vats. It may pass through a refrigerating apparatus on its way thither if it is preferred that it should do so.

Zimmermann and Holzwich's Process.

All apparatus or utensils which come into contact either with raw or with boiled linseed oil must be made of, or lined

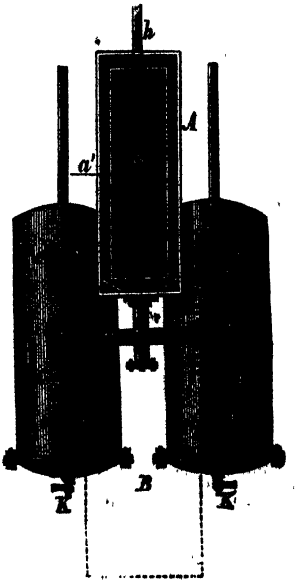


Fig. 12.

with, lead, because we thereby save adding litharge to the oil. The linseed oil used must be of good pale quality, and have been air bleached, if a pale boiled oil is expected. The boiled oil is made by an apparatus represented in figures 12, 13 and 14. Fig. 12 is a bird's-eye view; fig. 13 a vertical section, and fig. 14 an elevation. The apparatus consists of three main parts, *viz.*, (1) a box, A, of black sheet iron for heating the linseed oil; (2) an iron receptacle, B, lined with lead,

and (3) two closed iron boilers, CC, lined with lead. The oil flows from B through the cock F and the funnel *g* into the uppermost box *a*, passes then through the opening C into the box *a* directly underneath, and so through all the boxes *a a*, etc., till it gets into the lowest box *a*. Thence it passes through the tube *dd*, and the branch tube there-

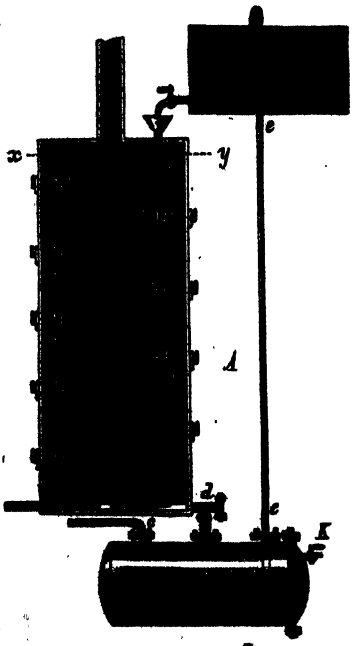


FIG. 13.

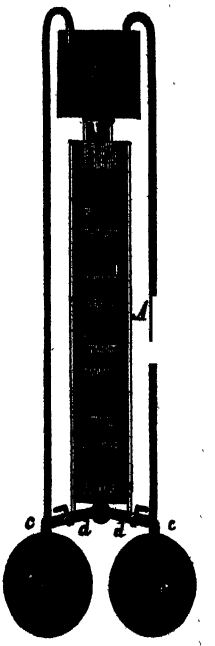


FIG. 14.

from, *dd*, which is provided with cocks, into one of the iron cylinders, CC, lying below. The air in this escapes by the air-cock *k*, which must be kept open during the filling. When such a boiler, C, is filled with linseed oil, the oil is pumped back again up into the reservoir through the leaden pipe *e*, and travels the circuit from A to C over and over again, till converted into boiled oil. The pumping is done

by compressed air, forced by an air-pump into the cylinder of oil, and which drives the latter up the tube *ee*. Two boilers are hence necessary for continuous work, so that one can be being pumped out while the other is being filled. The combination of this apparatus with the melting apparatus is with the object of utilising the air, which escapes at *x* at a temperature of still about 130° C. for heating the linseed oil. This air passes through *h* into A, where it helps heat up the oil passing through to the temperature required. We recognise by the consistency of the oil arriving in B out of C how far the process has gone, and whether the oil has to be sent round again. The handles, *b*, in the sides of the box, A, are stoppers, whereby it is made possible to inspect the surfaces, *a a*, over which the linseed oil runs, and to clean them when necessary. To lead off the vapours arising from the boiling oil, which are bad for the eyes, we have the adjustable valve *i*, which leads these combustible gases into the chimney.

A German Patent Process.

The object of this invention (D.R.P. 12,825) is to convert linseed or other drying oil into boiled oil by exposing it to the action of hot air until it has acquired a syrupy consistency.

Fig. 15 is the ground plan, fig. 16 a view and partly a section of the apparatus used for the treatment of oil. AA is a series of reservoirs to receive the oil. Each of these can be supplied with hot air by the tubes BBB. These air tubes are divided into radiating branches, which are so arranged that they hang directly over the bottom of the reservoir, without however touching it. These branch tubes are perforated, so that the air conveyed by them passes in thin streams through the oil. The tubes B of the various reservoirs are connected with a tube, B′, which is provided with hot air straight from the coil C of the heater D.

The coil C is connected with a pressure pump E (a Root's blower is to be recommended), to drive the air on its course.

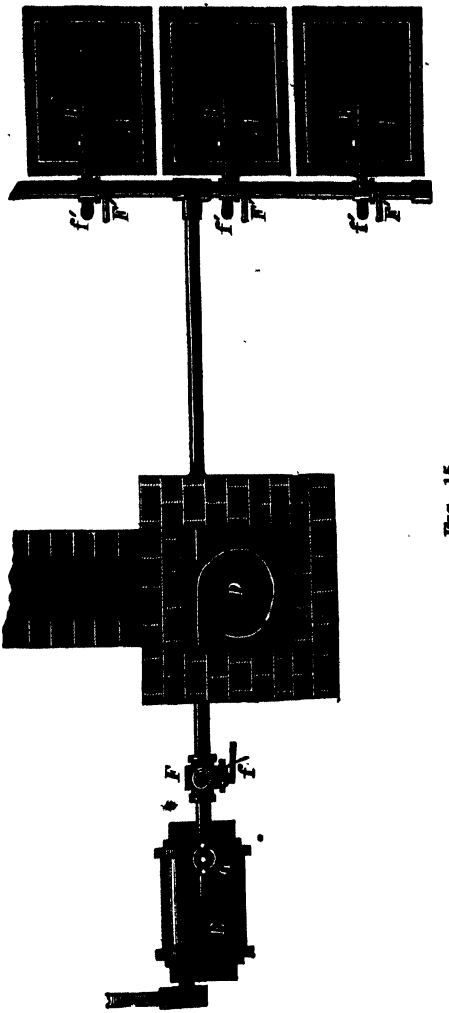


FIG. 15.

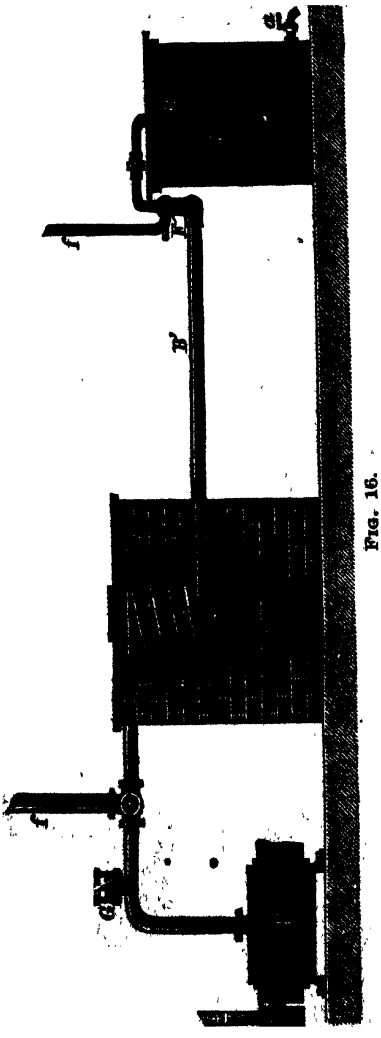


Fig. 16.

T is a cock to regulate the amount of air supplied to the coil by the blower. G is a loaded safety valve; the branch tubes, BBB, are provided with similar cocks, F, for regulating the supply of air to the individual oil reservoirs, and to cut off the air from each as soon as the operation is concluded in it. The cocks F and F' are three-way cocks, of a construction shown in fig. 17. They are so arranged that they can pass either all or part of the air current away into the open air.

If, for example, all the reservoirs are in use together, the supply of air must be at a maximum, and if the air is heated to about 312° C. the cock F must be partly open. If the temperature of the air issuing from the coil is above 312° C. the cock must be wider open, so as to lead less of the air from the blower into the exhaust-pipe F and more into the coil. By this, taking more air into the heater, burning of the oil is

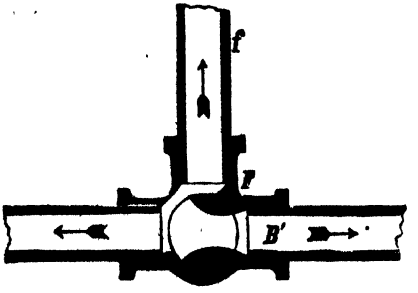


FIG. 17.

prevented. The temperature of the oil should never be above 205° C. It is most convenient so to arrange the process that the oil in different reservoirs is in different stages of progress, so that the reservoirs can be emptied singly and refilled when the process is finished without interfering with the work of others, and so a continuous action of the battery is ensured. As soon as the treatment of the oil in one reservoir is finished, the cock F' is turned, the supply of hot air is cut off, whereby it is prevented that the temperature of the oil in the other

reservoirs should be made too great. If, for example, the reservoirs contain 227 litres, so much hot air is passed into it as will raise the temperature of the oil to about 120° C. This temperature is kept up for about five hours, and it is then raised to about 205°, taking care however that this latter temperature is not exceeded. It is maintained in its turn for from five to six hours, to drive off the sharp vapours. As a sign of the conclusion of the process, the cessation of the evolution of these fumes serves very well. When they cease to come off, the oil thickens suddenly

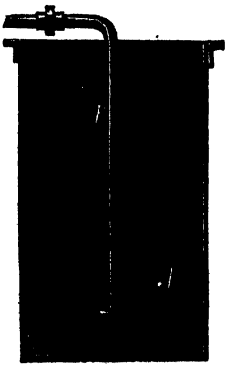


FIG. 18.

to a syrupy consistency. When this point is reached, the hot air is turned off, and the oil is run through the cock *a* into the storage vat. When cold the oil is quite free from the fatty substances and has the appearance of a pale jelly. The vapours expelled consist principally of oleine. They can be condensed and collected for the various uses of that substance. Fig. 18 shows a modification of the pipe bringing the hot air into the oil. Here the pipe ends in a T piece, not perforated at the sides, but open at each end, so that the hot air passes through the oil in two streams. This form is used with oil-holders, which are about twice as long as they are wide.

CHAPTER X.

ADULTERATIONS OF BOILED LINSEED OIL.

ALL boiled oils are subjected not only to a very large number of different kinds of adulteration, but in their manufacture such methods and processes can be resorted to as to have an unfavourable effect on the quality of the oil, and are adopted for various reasons, chiefly, of course, for the purpose of diminishing the cost of production.

Good boiled oil can only be got by boiling pure stocked linseed oil at a temperature not below 132° C. under the action of oxygen. It is indifferent whether this temperature is produced by a naked fire or by steam, and whether the oxygen is added through the agency of chemical compounds of oxygen, or by the introduction of air or pure oxygen. Boiled oil is, as has been said more than once already, oxidised linseed oil. It is in the main more or less decomposed linoleine containing the anhydride of linoleic acid, while it contains glycerine in the undecomposed portion of the linoleine. According to the duration of the boil there are present more or less oleine, palmitine and myristine, and the longer the boil the more the linoleine is changed into linoxyn and the quicker the oil will dry. Hence the nature of the boiled oil depends upon the boiling time, and also on the amount of oxygen incorporated with it both the rapidity with which it dries and the durability of the coats which it forms.

A good boiled oil must be somewhat thicker than the raw oil, but must not be too thick, or it will become necessary to thin it with oil of turpentine before it can be painted with in

thin coats. If it can only be applied thickly the coats never dry through, and the paint is sure to crack sooner or later.

The colour of boiled oil depends on its manufacture, and as a rule is pale or brownish yellow or reddish brown, never dark brown. Boiled oils prepared with the help of steam are usually paler than those boiled over a naked fire, and are manganese-prepared oils more usually than lead-prepared oils, and come nearest in colour to the products oxidised by air or oxygen. The duration of the boil is also not without influence on the colour. The longer the boil and the higher the temperature the darker the oil, from the carbonisation of the solid organic substances suspended in it.

Many makers of boiled oil heat the oil for too short a time, to save expense of manufacture, and so put upon the market a badly drying product. Such oil is generally very pale for boiled oil, but dries nearly as slowly as the raw oil and does not fulfil its purpose properly. Such a product can only be detected by comparing the time it takes in drying with that of an oil known to be satisfactory, by painting with both at the same time and drying under the same conditions.

The smell of good boiled oil is that of linseed oil with a slight scent of burning, such as that characterising the vapours evolved from the boiling oil. It may be unpleasant but it should in no case be nauseous, or have any resemblance to the odour of resin oil or fish oil; if it has it is probably adulterated with these oils, a conclusion which can be confirmed by the tests given below. If the boiled oil has been burnt by overheating, the fact betrays itself by an empyreumatic and nauseous smell, and a dark and dirty brown colour.

The taste is a good test of a boiled oil. In a good oil, except that it is bitter and more disagreeable, it resembles that of the raw oil. Adulteration with fish or resin oil is detected more quickly and certainly by the taste than in any other way.

ADULTERATIONS OF BOILED LINSEED OIL.

Boiled oil must be clear, without being rendered turbid by suspended solid matter. If it is not clear, it must be left for at least a fortnight at perfect rest in a fairly warm place. In this time it will have become quite clear, unless it is adulterated with resin oil, and the amount of sediment will show whether the oil is good or bad. Even well-stocked boiled oil gradually deposits, but even after months the sediment will not exceed ½ per cent., and is not worth taking into account. Many makers, however, only give the boiled oil time to clarify superficially, and sell it a few days after it is made. Such oils come turbid to the consumer. They will certainly clear if he will keep them for from two to four weeks, but the amount of sediment may amount to 7 per cent., and the boiled oil must be considered as of very inferior quality.

The drying power is one of the chief tests of a boiled oil. It ought to dry in thin coats on wood, glass, or metal, in twenty-four hours to such a point that although still sticky it cannot be wiped off, and in another twenty-four hours it ought to have dried solid, retaining, however, some elasticity and softness. If it dries quicker than this, so much the better, but if it dries slower, that is a sign that it has either been improperly prepared, or that it is adulterated. It is possible that it has never been boiled at all, but prepared by cold processes, *i.e.*, by being mixed with from 6 to 10 per cent. of the so-called "extract". Such a product has no claim to be called boiled oil, for to make that a high temperature and the addition of oxygen are both indispensable, and cannot be replaced by mechanical admixture of the linseed oil even with the strongest driers.

The commonest adulterants of boiled oil are colophony, resin oil, and fish oil, all having the single object of lowering the cost of production and of offering under the temptation of a lower price an article which only in the rarest cases will answer the expectations of the buyer. All the above adul-

terations radically affect the drying power. Boiled oil adulterated with colophony and resin gives coats which after any period become sticky with the heat of the hand, and in spite of their softness soon come off. Boiled oil adulterated with fish oil will not dry at all and is absolutely unusable. The adulterations named may be detected by the following means.

Colophony.

Boiled oil adulterated with colophony is generally thicker than it ought to be. It dries in from thirty-six to forty-eight hours to an apparently solid film, which, however, becomes sticky by the heat of the hand laid upon it. The coats readily collect dust, and become grey and dirty, and exposure to the weather soon destroys the coat, which crumbles away. If we shake up boiled oil suspected of adulteration with colophony with 95 per cent. spirit at frequent intervals during a few hours, and then allow the mixture to stand, the colophony can be detected in the tincture after decanting off. To effect this the tincture is distilled till all the spirit has evaporated. This point is easily recognised if the spirit was weighed before use, by the weight of the distillate. If the residue has more than one-fortieth of the spirit the adulteration is resin if the residue is solid, resin oil if it is liquid. The result is of course quantitative, and the nature of the adulterant can be confirmed by appealing to its smell and taste.

A somewhat more complicated test for colophony is to boil the oil for a few minutes with 95 per cent. spirit, draw off the spirit when the mass is cold, and add to it a solution of acetate of lead. If the oil was pure, the result is a turbidity merely, but if it contained colophony we get a clotted white precipitate which by repeated washing and fusing can be converted into pure colophony.

Resin Oil.

Resin oil is the commonest of all adulterants of boiled oil, and can be detected in most cases simply by its smell. The

resin-oil smell becomes more distinct if a few drops of the oil are rubbed between the palms of the hands until it is warm. Taste affords also an excellent means of detection to any one who knows the characteristic rough and nauseous taste of resin oil, of which very small quantities may be at once and with certainty detected by this means.

If boiled oil containing resin oil is mixed with dilute sulphuric or hydrochloric acid, shaken, and then left to stand, these show themselves in the white lead or manganese precipitates formed, whitish sticky lumps, while with pure boiled oil only the first-mentioned precipitates appear, and the oil appears fully cleared in a few hours at most. The oil-hydrometer can also be used. Pure manganese-boiled oil shows 26° and lead-boiled oil 24°, while the adulterated oil will be from 20° to 22° only.

Fish Oil.

Adulteration with fish oil may also be detected both chemically and by taste and smell. If we mix ten parts of the suspected oil with three parts of sulphuric acid by stirring, and then allow oil and acid to separate by standing, there will be a white precipitate containing the metallic drier, and the oil will have assumed a dark brown, the acid orange-yellow or yellowish-brown colour, if fish oil is present. If on the other hand the oil is unadulterated, it will be green, turning later to a brownish green, while the acid has a nearly pure yellow colour. If the suspected oil is treated with pure chlorine, it will become dark brown at once, and black ultimately if fish oil is present. Unadulterated oil on the other hand is bleached more or less by the chlorine. Chlorine bleaches all vegetable fats, but turns all animal fats, with the single exception of neat's foot oil, darker and darker, and finally black. If boiled oil is mixed with one-fifth of its volume of caustic soda lye of

1·34 sp. gr. the emulsion formed is yellow with pure oil, but red if fish oil is present.

Other Adulterations.

When boiled oil is very dear we find occasional adulteration with turpentine, and even with benzole. If a few drops of the oil are rubbed between the palms of the hands, the smell of turpentine or benzole becomes recognisable. A more certain means, however, of detecting the adulteration is to distil the oil, when the volatile turpentine or benzole easily comes over, leaving the linseed oil in the still. If the amount distilled was first weighed the test can be made a quantitative one.

It is easy to see whether a boiled oil has been prepared by the use of lead manganese or other metallic drier. If the reagents employed to test for them give negative results, *i.e.* no precipitates, we can only conclude that the oil was prepared with oxygen or atmospheric air. All oils prepared with metals contain linoleate of whatever metal has been employed, and if dilute sulphuric or hydrochloric acid is added to the oil, the metal is either dissolved by the acid or precipitated, and in either case is separated from the oil.

The oil to be tested is mixed with about its own volume of dilute sulphuric acid, and notice is taken whether a precipitate forms or not. If a white precipitate goes down, and turns black when treated with sulphuretted hydrogen, the boiled oil contains lead. If no precipitate is formed, but the acid becomes itself somewhat coloured, and blackened by the subsequent addition of sulphuretted hydrogen, the oil contains copper. If the sulphuric acid precipitate is not blackened by sulphuretted hydrogen, no lead is present, and further testing must be resorted to, first with ammonia and then with sulphide of ammonium. This reagent gives a black precipitate in the presence of iron, a flesh-coloured one with manganese, and a white one with zinc. Further in-

formation is obtained if we treat the original acid solution with a solution of carbonate of soda in water. If this gives a dirty green precipitate, which soon turns black on exposure to the air, iron is present. This may be confirmed by treating the acid solution with ferrocyanide of potassium, which gives a blue precipitate with iron. A white precipitate with the carbonate of soda, turning dark brown in the air, shows manganese. If zinc is present, the acid solution from the boiled oil will give with ammonia a white precipitate, readily soluble in excess of ammonia.

W. Fox has made known a process for detecting raw linseed oil as an adulterant of boiled oil. It is based upon the decomposition of the oil on boiling, the fatty acids being oxidised and the glycerine forming compounds with acrylic acid, which escape and cause the well-known smell.

Oils are frequently put on the market either consisting of boiled oil adulterated with raw oil, or more frequently of raw oil containing a little liquid siccative. Such products have naturally comparatively small drying power. To test for glycerine, 5 grammes of the oil are saponified in the usual way, the soap is decomposed by hydrochloric acid, and, after standing, the acid liquid containing the glycerine is run off from under the layer of fatty acids, made strongly alkaline, and then mixed with crystals of permanganate of potash till the solution remains a light red. The excess of permanganate is next decomposed with a little sodium sulphite, the precipitated peroxide of manganese is filtered off, and the filtrate is made acid with acetic acid, raised nearly to boiling, and then treated with solution of calcium chloride. If this forms a white precipitate, glycerine was originally present and has formed oxalic acid according to the equation :—

$$C_3H_8O_3 + 3O_2 = 3H_2O + CO_2 + H_2C_2O_4.$$

The oxalate of lime can be converted into carbonate by ignition, and weighed. Every 100 parts of the carbonate correspond to 92 of glycerine.

CHAPTER XI.

CHINESE DRYING OIL AND OTHER SPECIALITIES.

In making Chinese drying oil by H. X. Busse's patent, coarsely but uniformly powdered bone-charcoal, previously purified with hydrochloric acid, is placed in a narrow-necked funnel, and old stocked linseed oil is filtered through it into large shallow pans of lead containing crystalline basic acetate of lead, red lead, and borate of manganese. The mass is exposed to diffused daylight under glass plates, and the leaden pans are kept at 120° C. for six hours, while a stream of air at the same temperature and containing 16 per cent. of steam is passed through them. The oil is then placed in shallow leaden dishes which are piled up in large closed iron cylinders, so as to allow free circulation of air over all the surface of the oil. In the upper part of the cylinder is placed a wide-necked flask containing chloroform, 2 kilos. of this for every 50 kilos. of the prepared oil. A current of air at 100° C. is then passed through the cylinder from above downwards, issuing from a regulatable valve. After eight to ten hours the oil becomes thick and tough, and it is then heated with American oil of turpentine, first heated to 300° C. in closed vessels with 10 per cent. of its weight of absolute alcohol. This mixture is allowed to cool to 100° C. and is then mixed with its own weight of the thickened oil.

The yellow solution formed is at first turbid, and is allowed to clarify at a low temperature in iron containers.

If a little of this drying oil is added to linseed oil or to an oil-paint it gives it the best drying qualities. On standing

it removes all vegetable albuminous bodies from drying oils. With linseed oil it gives a straw yellow mixture which dries in from eighteen to twenty-four hours to a tough india-rubbery elastic coat.

Cement-Boiled Oil.

By the process of C. Neumann (D.R.P. 25,139) a cheap durable and paintable varnish, soluble in water, and intended to replace ordinary boiled oil for all purposes is manufactured. It consists essentially in partly saponifying oil and resins, or solutions of them both, with water-glass, then boiling, and completing the saponification with ammonia. The varnish is separated out by adding a concentrated solution of alum and chromate of potash, and after dilution with water is ready for use. To explain the process more exactly, the following description is given of the manufacture of cement-boiled oil. The ingredients may naturally be replaced by others of similar nature without any of the steps of the process requiring modification.

For the preparation of 500 parts of the preparation we treat 16 parts of Portland cement with 160, or 16 per cent., potash lye. After five to six hours the insoluble lime compounds have settled to the bottom, while the silicates in the cement have gone into solution, forming water-glass with the potash.

The lye, which has become about 4 per cent. heavier, is now boiled for about two hours with 100 parts of linseed oil and 40 parts of Burgundy pitch. At the end of this time 40 parts more of lye are added, but 20 per cent. lye this time, and the boiling is continued for another half-hour.

The hot lye saponifies the greater part of the Burgundy pitch and the oil, and the saponification is now finished by stirring in about 4 parts of alcohol and 3½ parts of ammonia.

By this saponification an extraordinarily intimate com-

bination or mixture of the material is secured, so that a very homogeneous product is obtained.

Next we prepare a concentrated solution of 4 parts of alum and 1 part of bichromate of potash, which is diluted till the hyacinth-red colour changes to a chrome yellow. This fairly consistent solution is gradually stirred into the above saponified mass, till the result is a fairly thick mass of a clear brown colour.

This mass is then treated with 400 parts more, and the whole is again boiled up. The product is then ready. The addition of the salt solution causes on the one hand a coagulation, effected by the chromic acid, and on the other a formation of palmitate of alumina by the action of the alum on the fats or resins. This palmitate of alumina dissolves in the ammonia present, but when the varnish dries becomes insoluble, and so produces a durable coat.

Carbolic Varnish.

To make a preservative varnish for painting wood, so as to keep it from mould and dry rot, and also for painting over walls which show growths of mould, dissolve in an iron kettle 10 lb. of borax and 5 lb. of caustic soda in 40 gals. of water. Then boil, and while boiling stir in 45 lb. of shellac. When the shellac is dissolved, let the solution cool till it is lukewarm and then add 20 lb. of 90-95 per cent. carbolic acid. This varnish is applied lukewarm, and according to the material to be painted with it is diluted with hot water up to about one-third of its volume. This varnish is perhaps a substitute for carbolineum.

Tar Varnish.

In a box heated by a steam pipe or in a pan over a fire keep 40 kilos. of tar at 70° C., with constant stirring for some time to dry it as far as possible. Then stir in, keeping up

the temperature, 40 kilos. of hydraulic lime or 6 of Portland or Roman cement. The mass gradually becomes saponified, and in spite of the large amount of cement added to it remains quite liquid, and even when cold it is soft and smeary. It is ready for use except that it has to be used warm. If it is attempted to use ordinary quicklime instead of hydraulic lime, even 25-30 per cent. of it added to the tar will at once solidify it so that painting with it is impossible. By the saponification of the tar by the cement the volatile oils of the tar are retained, so that a varnish is got which resists weather perfectly, while ordinary tar weathers off in time.

Neither hydrochloric nor nitric acid attacks the tar-varnish above described, and it will not only resist the weather but mould. It is thus excellent for woodwork exposed to water or in places where it is subject to the attacks of mould or dry rot.

The tar preparation has also the property of drying soft so that the coats cannot crack or get brittle. It is a good application for roof-tiles, and prevents them from being damaged by frost, as they are made waterproof. It is also good for earthenware pipes.

CHAPTER XII.

PIGMENTS FOR PAINTERS, ARTISTS AND PRINTERS.

PIGMENTS come from all the three natural kingdoms, animal, vegetable and mineral. Some of them occur ready-made in nature, while others are manufactured from natural or artificial raw materials or both. On the whole they may be classed as:—

1. Inorganic or mineral colours.
2. Organic colours.
3. Mixtures of the two.

The value of all pigments depends upon the following properties, or on the extent to which they are possessed:—

1. *Shade of Colour.*—The purer this is, *i.e.*, the nearer it is to the spectrum colour, the better. The shade is always estimated by comparison with a standard sample.

2. *Body or Intensity.*—This is determined by seeing how much of the pigment is needed to give the same result as a given quantity of the standard pigment, of course on a surface of the same size as that to which the standard has been applied.

The body of glazing colours can be determined colorimetrically, by dissolving equal weights of a standard colour and that to be tested in equal weights of the same solvent, and comparing the heights of two columns, one of each solution, which give the same intensity. The body is inversely proportional to the depth of liquid required to produce any given intensity of colour. Another plan is to dilute the two solutions till their intensity of colour is the same. Then the

body of the pigment under test is to that of the standard inversely as the quantity of each present. Two simple glass burettes of equal size answer for this kind of test. Into one is put a known quantity of the pigment to be tested, into the other the same quantity of the standard. The deeper is then diluted with the solvent till it has the same intensity as the other. Then if, for example, the volume of the standard liquid is twice that of the other, the standard pigment has twice the body of the other.

Another method, chiefly used for body colours, consists in mixing the finely powdered pigment with a white solid having no action on it, and comparing the colour of the mixture with a similar one made from the standard pigment. A good substance to use for this purpose is kaolin or white porcelain clay. Stein carries out the test by adding kaolin, 5 grammes at a time, to 500 grammes of the pigment under test. If the hue is different for the same quantity of kaolin, the bodies of the two pigments are different. In this case the deeper is mixed with more kaolin till both are the same. Then the respective bodies of the two colours are in the same proportion as the two total amounts of kaolin added to them.

3. *Fastness.*—Many pigments behave very differently to air, light, soap, alkalis, acids, bleaching agents, etc. The greater the resistance offered by a colouring matter or an object coloured with it to the above agencies, the faster the pigment is. There are great differences in the amount of fastness expected according to the purpose to which the colouring matter is to be applied. For example, artists' pigments have to be permanent for many years, while a green or yellow pigment intended for house-painting will have lost its colour partially or entirely in only a few years.

It cannot of course be considered a part of my duty to give descriptions of the manufacture and use of every colouring matter used, because such information must be sought in special books, such as Bersch's *Fabrikation der Mineral und*

Lack Farben, Fabrikation der Erdfarben, and *Fabrikation der Anilinfarben* (published by A. Hartleben, Vienna and Leipzig), where it will be found exhaustively given. I confine myself to mentioning the separate categories, each with its chief representatives, and to showing how the consumer can test them for fastness and purity. It is clear that this cannot be done exhaustively, and for those who wish still further information I recommend Dr. Dammer's *Lexicon der Verfalschungen*, of which I have partly made use in writing this part of my book.

The categories are as follow: colours of antimony, arsenic, barium, lead, cadmium, chromium, iron, cobalt, copper, manganese, mercury, zinc, animal colours and vegetable colours (lake-colours).

Antimony Colours.

Antimony cinnabar gives with oils a fine red colour. It is soluble in hydrochloric acid, but insoluble in other dilute acids, and is destroyed by alkalis.

Arsenic Colours.

Realgar, red arsenic, ruby sulphur, are hardly used now, and orpiment.

Barium Colours.

Heavyspar is in pigment manufacture a much used addition to colours. As the body of finely ground heavyspar, especially in oil, is very small, pigments mixed with it lose considerably in value, and every addition of heavyspar not distinctly revealed by the manufacturer must be regarded and treated as a fraud. In the case of those pigments which cannot be made without heavyspar, such as Victoria green, the quantity of heavyspar is generally guaranteed by the manufacturer.

Heavyspar is distinguished by its inactivity and its in-

solubility in acids or alkalis. These properties, together with its white colour, make it very suitable for toning down dark shades, or for making cheaper white pigments with white lead, lithopone, or zinc white. The colour of heavyspar is a very important test of its quality. The whiter and the finer ground it is the better. As many varieties of heavyspar contain gypsum or celestine (strontium sulphate), we often find these bodies in the ground heavyspar of commerce without being able to regard them as adulterations. Besides gypsum and celestine, natural heavyspar almost invariably contains oxide of iron, alumina, and silica, but not as a rule in important quantities.

Lead Colours.

White lead varies in body according to the method of preparation, *i.e.*, according to its molecular constitution. That made by the Dutch method has more covering power than English, which again has more body than French white lead. White lead leaves the factory: (1) Finely ground; (2) In shaly leaves (shale-white), as it is got by hammering the leaden sheets; and (3) in quadrangular or conical lumps made by moulding or pressing a paste made by grinding the pigment with water.

White lead is largely adulterated with inferior mineral whites, especially heavyspar, and sometimes with chalk, gypsum, clay and sulphate of lead. These additions show themselves as insoluble residues when the white lead is dissolved in acid. Chalk, however, may dissolve with the white lead, so to test for it we precipitate the lead from the solution by means of sulphuretted hydrogen, and test the filtrate, after evaporating it and driving off the sulphuretted hydrogen, for lime.

Naples yellow, a yellow pigment for artists: not known to be adulterated.

Red lead, Paris red or lead red, is a scarlet red for oil painting, and is often adulterated with brickdust, red ochre, red oxide of iron, heavyspar, gypsum, sulphate of lead, clay, and sand. Unadulterated red lead will dissolve on heating in a solution of sugar containing nitric acid, with evolution of carbonic acid, but the above-named adulterants remain undissolved.

Cadmium Colours.

Cadmium yellow is a yellow pigment for artists and printers. It dissolves in concentrated hydrochloric acid, which leaves adulterations undissolved. It is not affected by sulphuretted hydrogen or ammonium sulphide, but chrome yellow is destroyed by them.

Chromium Colours.

Chrome green, Guignet's green, permanent green, chrome hydroxide, Victoria green, oil green, chrome colours in a pure state, are only used by printers. By mixing them with other pigments a whole series of greens is produced. If we mix pure chrome green with a white, such as gypsum, heavyspar, or clay, to make the shade lighter, we get shades verging into greyish blue, and which by the addition of a little pure yellow, such as chrome yellow, or chromate of zinc or barium, become very warm. These greens can only be regarded as adulterated with the whites when they are described as chemically pure. Purity is tested by fusing the pigment with soda and saltpetre in a platinum crucible, when the chromium passes into a soluble alkaline chromate, while the sulphuric acid and the heavyspar forms sulphate of soda, and the barium remains insoluble as chromate or carbonate. The insoluble residue after washing on the filter, can be tested for barium by dissolving it in cold dilute hydrochloric acid, and adding solution of calcium sulphate. The formation

then of a white precipitate or turbidity shows the presence of barium. The blowpipe flame of barium is green. Chrome yellow, chrome orange, chrome red, yellow pigments of from the palest lemon yellow to the deepest cinnabar red; the colouring substance of the yellows is neutral lead chromate, that of the oranges and reds basic lead chromate. They answer for house painters, artists and printers. Of real adulteration with sulphate or carbonate of lead, lead spar or gypsum, it can only be a question when they are added without being allowed for in the price, for chemically pure lead chromates are useless as pigments. Unless mixed with other materials they always change colour and spoil. These other materials may be added to the extent of 60 per cent. or even more. Barium yellow has almost gone out of use

Zinc yellow, yellow ultramarine is chiefly used by printers. It is distinguished from chrome yellow by not being precipitated black from solution in hydrochloric acid. For house painters and artists.

Iron Colours.

Paris blue, Berlin blue, Turnbull's blue, for house painters, artists and printers. The best pigments are the pure steel-blues (Milori blue, steel blue, bleu d'acier) and those which show a coppery lustre. Pure Paris blue is mixed with starch, heavyspar, kaolin, or gypsum, partly to cheapen it and partly to get lighter shades. Much more of the lighter adulterants can be added than of heavyspar, and the value of the pigment depends simply upon how much Paris blue it contains. The testing to ascertain the same is rather troublesome. Turnbull's blue is distinguished from Paris blue by being made by precipitating a ferrous instead of a ferric salt.

The iron colours include the numerous pigments found ready made in nature which have oxides of iron as their main essential constituent, such as ochres, bole, Siena earth, Pozzuoli earth, etc. As these pigments occur ready-made in

nature, so that nothing can be said about any admixture of particular foreign bodies, chemical investigation, pure and simple, gives no idea of their value.

The testing of them depends, therefore, mainly on seeing that they are finely ground and free from coarse particles, especially of sand, which show imperfect levigation. The colour is of the greatest importance and the warmer and more beautiful it is the more valuable the pigment. The various shades are partly provided by nature, but are in many cases got by the use of artificial heat. Of late, aniline dyes have been used to enhance the fire of ochres and various other red mineral colours. Ochres so treated, however, gradually turn pale when exposed to light, and nothing is left in time but the original colour of the ochre. Such falsification is readily recognised by dissolving out the dye with alcohol or water, in one of which the dye will dissolve, and then filtering the solution from the insoluble earth.

Cobalt Colours.

Smalts, Thenard's blue, coeruleum, Rinmann's green. Smalts is a blue cobalt glass, but is not now much used, and Cobalt or Thenard's blue has been almost completely superseded by ultramarine. It is still used, however, in porcelain-painting and by artists in oils. Rinmann's green is not even manufactured now.

Copper Colours.

Mountain blue, mountain green, Brunswick green, Bremen blue, Scheele's green, Schweinfurt green.

Mountain blue and green occur in nature and are also made artificially. They are constantly adulterated with heavyspar or gypsum.

Brunswick green, used as an oil pigment, is adulterated in the same way.

Scheele's or mineral green contains arsenic. The most important copper-pigment is:—

Schweinfurt green, a compound of copper arsenite with copper acetate. The darker shades are more crystalline than the paler ones, and for this reason have less body. To detect admixtures of gypsum or heavyspar a weighed quantity of the pigment is treated with hydrochloric acid, the excess of acid is removed by evaporation on the water bath. The whole mass is then mixed with twice its volume of strong spirit. After twelve hours' standing the sediment is filtered off, washed on the filter with a mixture of 2 vols. of alcohol and 1 vol. of water, dried, ignited and weighed. The spirit may be omitted throughout if gypsum is not present.

Manganese Colours.

Browns, such as umber, chestnut brown, roe-brown, etc., which are not made artificially, but are dug from mines. They owe their colour to compounds of iron and manganese and are the less valuable the more earthy impurities, such as clay, are mixed with them. By roasting at particular temperatures, levigating and grinding, the natural products, which chiefly occur in beds of iron ore, are made of very beautiful brown hues of good body. The pigments must be judged by their colour and body, and tested for artificial dyes with alcohol or water as described under the head of iron colours.

Mercury Colours.

Cinnabar is the only pigment made for all purposes. It is adulterated with brickdust, oxide of iron, red lead, chrome red, cinnabar imitation, and red coal-tar dyes. The first four remain behind when cinnabar is volatilised by heat. Cinnabar imitation is red lead or chrome red plus eosine. Lead and chrome remain behind in the residue after heating and eosine is extracted, before heating, with alcohol.

Zinc Colours.

Zinc white, zinc grey, lithopone.

In testing zinc white we usually confine ourselves to testing the solubility in acid and alkali. The usual adulterant is heavyspar, which remains undissolved in either case.

Zinc grey is zinc oxide mixed either with the metal or with finely powdered charcoal, or is ground blende (zinc sulphide). Its value depends on its colour and body. Lithopone is a mixture of zinc sulphide, zinc oxide and heavyspar. It may be adulterated with chalk to make it give a larger proportion of matters soluble in acids, the chalk being then taken for zinc oxide. We should never omit to heat a solution obtained from the lithopone by strong nitric acid with ammonia in excess. This ammonia should give no precipitate, showing the absence of iron and alumina. When satisfied on this point, we make the solution acid again, but with acetic acid, and precipitate the zinc with sulphuretted hydrogen. The filtrate is tested with oxalate of ammonia for lime, and with sodium phosphate for magnesia.

Carmine.

The colouring matter of cochineal is subjected to many adulterations, on account of its high price. Among them are starch, clay and brickdust. As pure carmine is completely soluble in ammonia, which dissolves none of these things, falsification is readily detected by the use of that reagent.

Carmine lake, Munich lake, cochineal lake, Florentine lake, etc., are made by precipitating a decoction of cochineal with alum and alkali. Mineral adulterations are found by burning and examining the ash.

Lake Colours.

Under this title we understand colours obtained by precipitating organic dyes on minerals such as heavyspar, clay,

gypsum, etc. There is an enormous number of such pigments: madder lake, garancine lake, carmoisine lake, Vienna lake, ball lake, Venetian lake, cochineal red, purple lake, gamboge lake, blue lake, green lake, etc., etc. They are beautified by the addition of aniline dyes, and also with large quantities of mineral matter or starch.

Indigo

Is adulterated with mineral matter, starch, gums, glue, sugar, dye-extracts, Prussian blue. It is very little used in oil-painting.

Frankfort Black.

This is made by charring grape-stalks and other vegetable matter. Its value depends on its colour. The less brown there is about it the better. Good vegetable black must, when burnt, leave hardly any ash. It is largely adulterated with wood-charcoal, which cannot be detected chemically. Adulteration with ordinary coal has also been noticed.

Bone black and ivory black are black pigments of various fineness and depth, according to the raw material. They are got by heating bones with exclusion of air. They are hardly likely to be adulterated with mineral substances and such could be easily detected by burning and testing the ash.

CHAPTER XIII.

PIGMENTS FOR PRINTERS' BLACK INKS.

THE chief pigment for printing ink is now, as it always has been, lampblack, obtained by burning organic substances rich in carbon. It is the most suitable body for the purpose, on account of its fine black colour, its small weight, and many other advantages. Many attempts have been made to oust it from its position, but no satisfactory substitute has so far been discovered.

Printers' ink consists of boiled oil and pigment only. It is not sufficient for the manufacturer to take pains in the making of the vehicle, and in the amalgamation of it with the pigment; he must see to it that his pigment is satisfactory, and to escape trouble and to be able to meet competition it is essential that he should not purchase lampblack, but make his own. It is true that the various makers offer very fine and praiseworthy products, but you can never be sure of getting the same quality twice. The printing-ink maker, in order to be able without fail to make the same ink at different times with the same vehicle, should be able to make a pigment of the same quality in every batch. If, for example, a lot of lampblack is lighter and flakier than the last, it will make a thicker ink for the same quantities. If the change is of the reverse kind, the ink will turn out thinner, and in both cases the customer is dissatisfied. As a matter of fact the cardinal principle that a printing-ink maker should manufacture his own lampblack, and make himself independent of the market article, is now recognised in all large printing-ink factories.

For the manufacture of lampblack a very varied selection of raw materials is employed, such as American resin, ozokerite, and the hydrocarbons got as bye-products in the refining of petroleum and the distillation of brown coal. Besides these fish oils and vegetable oils in a fresh or rancid state, light and heavy tar oils, wood-tar oils, supply raw materials very suitable for lampblack manufacture, being readily combustible and rich in carbon. With regard to the vegetable oils it should here be mentioned that it is advantageous to use them when they are very rancid, as they then give a greater yield of the black pigment. The reason of this is that a rancid oil requires a freer air supply to burn without smoke than the same oil in a fresh condition. This circumstance also shows that a part of the carbon of the rancid oil requires a higher temperature for its combustion than is the case with a fresh oil. Hence the use of rancid oil in lampblack making has a double advantage. It not only gives a larger yield, but is cheaper than fresh oil. There is only one disadvantage attending the use of rancid oil, and it is not one of great importance. It is that the oil, on account of the large quantity of free fatty acid which it contains, rapidly corrodes the metallic parts of the lamps in which it is burnt, especially in the case of copper or brass. Hence it is best to avoid copper and brass as much as possible in making the lamps, and to make as much of them as possible, especially the oil reservoir, of tinned iron.

Of the tar oils got by distilling ordinary and brown coal, we have the heavy and the light, which differ not merely in specific gravity, but in boiling point, which with these oils varies within rather wide limits. They show great differences between the amounts of oxygen which they require for complete combustion, *i.e.*, for burning with a luminous and non-smoky flame. The more oxygen an oil needs to burn smokelessly, the better it is for lampblack making, as it is easier by restricting the air-supply to make them burn smokily.

Such oils may generally be recognised by possessing both high specific gravity and high boiling point.

The whole installation of a lampblack factory consists of two main portions, the room in which the combustion takes place, and in the arrangements for collecting the lampblack. In the newer processes of manufacture, of which we shall presently treat, the usual chambers for collecting the product are dispensed with.

It is advisable, as conducing both to uniformity of the product and to safety from fire, to make the receptacles for the lampblack entirely of brickwork, which should be well pointed to prevent too much lampblack lodging in crevices. The end of the lampblack channel should communicate with a high chimney provided with a well-fitting damper, so that the draught may be regulated at pleasure, or cut off altogether. Such a plant, although somewhat expensive, has a large number of important advantages. It is all of fireproof construction, and if it gets warm slowly, once warm it keeps its heat a very long time, because bricks are bad conductors of heat. Once the channel is hot, water ceases to condense in it, and all steam passes through it with the products of combustion to the chimney. Another advantage is that the lampblack channels do not often have to be entered. They can be cleared at wide intervals, and hence the combustion has only seldom to be interrupted. The lampblack collects on the walls of the passages in flakes which finally fall to the floor. There should be only one opening for emptying the the passages, and this must be provided with an iron door, which should be luted up except when the combustion is stopped, and the passages are being emptied. Unless this door can be closed air-tight it is futile to think of regulating the supply of air to the lamps by means of the chimney-damper. When it is necessary to clear out the lampblack, a workman goes into the passages with an iron pail and a soft brush, and gathers the lampblack off the walls and floor.

It is of the greatest importance that he should put nothing into his pail but lampblack. Hence his brush must be too soft to disturb the mortar of the brickwork, and he must wear felt slippers while at work, as nails or even leather soles to boots are apt to scrape foreign matter off the floors of the passages. The least bit of sand or hard stuff in the lampblack will do much harm in the subsequent processes.

The lamps for burning the raw material are of the most varied construction, and the same lamp will not do for every kind of combustible. Lampblack is usually divided into two kinds, flame-black and lampblack proper. For the first no lamps are used, and we shall describe its manufacture first.

Thenius's Oven.

Here the raw material is the last oil got in distilling coal-tar, and freed as far as possible from naphthalene. This is burnt in a special stove, represented in fig. 19. The com-

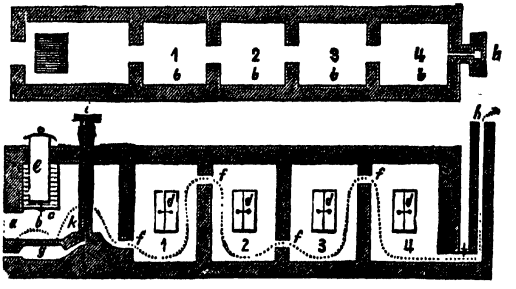


Fig. 19.

partment *a* contains an iron plate kept always red hot. On to it the oil drops from the tube *c*. The smoke resulting passes in succession through chambers 1, 2, 3 and 4, through the small openings *f*.

When enough pigment has been made, the oven is left for a few days, and the chambers are then entered by the

windows *d*. No. 4 contains the finest product, and that in No. 3 is very good. That in Nos. 1 and 2 is second quality only. Four hundred kilos. of the oil yield about 70 kilos. of black, about half being got from chambers 3 and 4. The iron plate is then cleaned, and the process is started again. The coke knocked off the iron plate is used for fuel.

Oven for Burning Asphalt.

The oven can be built of masonry or brickwork, but the inner room C must be lined with thick plates of iron. The doors *d* are also of strong iron plates and also the door *a*,

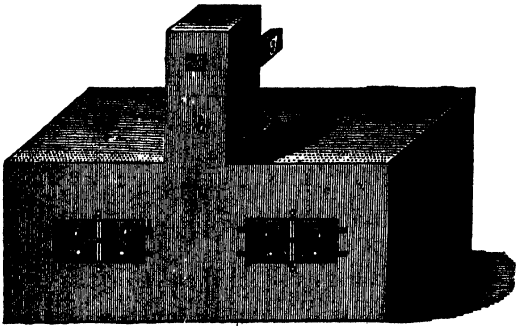


Fig. 20.

which has a few holes in it to admit the air required for combustion, but which can be closed at pleasure. The chimney C has at *g* a communication with the lampblack chambers, which are arranged as in Thenius's apparatus. In the oven asphalt or pitch is burnt with as little air as possible. The asphalt is fed in through the doors *a a*, and the lampblack passes into the chambers through the chimney and there it sorts itself according to its fineness. When the lampblack is to be removed, operations are suspended for a few days before the doors are opened. Five hundred kilos.

of smiths' pitch give about 200 kilos. of total lampblack. The coky residue has to be broken up with hammer and chisel. It amounts to about 200 kilos. and is used for fuel.

This oven will burn for the manufacture of black the various dry residues of the purification of raw oils and creosote. These residues may contain potash or soda but they are rich in oil and resin. They are used, however, not alone but mixed with the asphalt, as they do not burn well separately, although they give as good a black under the above conditions. When the chambers have been cleared out a wood fire is lighted in the oven to burn the black alkali-containing residues to a grey ash, which can be sold as a manure, when powdered after they have got cold.

Oven for Resin, etc.

Another oven for burning resin, pitch, ceresine, etc., is shown in fig. 21. The iron dish G stands in contact with the water in another G_1. This water must be replaced as it evaporates, as it has the important function of keeping the fused material in G from getting too hot. If that happened, a dry distillation would take place, the products of which would accompany the smoke, and spoil the lampblack, perhaps even reduce the product of the chambers to a smeary paste, which would have to be burnt all over again. The pipe R leads to the chambers, and the smoke and combustion gases enter it by the opening O. O is really a long slit only a few cm. wide, but reaching nearly the full width of the combustion chamber. The lid D is only removed to renew the supply of combustible. The supply of air is regulated by altering the position of a damper inserted into D. This, however, has to be assisted, for the necessary control over the air supply, by a damper in the chimney. In order that the progress of the combustion may be observed a glass window is provided. At the commencement of an operation the

damper in D is fully opened, and the chimney damper is regulated so as to produce a strong draught. As soon, however, as thick black smoke begins to come out of the chimney, we have a sign that the passages are full of the combustion gases, and that they are being regularly drawn through the flues. We then diminish the strength of the draught with the dampers until the chimney only shows a

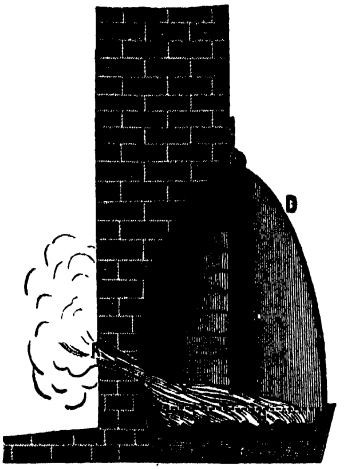


FIG. 21.

just perceptible smoke, and the flame in the combustion chamber becomes a dirty red instead of white.

Oils too can be burnt in this stove if a proper hearth is provided for them. These hearths are so constructed that while the surface is burning more oil is entering from below. As is the case with pitch or resin, it is indispensable that the hearth should be kept cold by a constant supply of water below it, or it would soon become so hot as to evaporate a lot of the oil, which would then escape combustion, and also make the flame very difficult to regulate.

Real Lampblack.

For burning liquid fats, such as train oil and vegetable and mineral oils, lamps are used. The construction of these is directed to the point that they shall burn no more carbon than is absolutely necessary to keep up the combustion. At the same time the temperature of the flame must be kept as low as possible to prevent it from burning any of its own smoke. The lamps have fish-tail burners and must be enclosed in an iron case provided with a damper, which must be very accurately fitted, or else air will get in through the crevices, and the use of the damper will become illusory. To prevent the fuel of the lamp from getting too hot, which would entail great loss by evaporation, especially in the case of mineral oils, the reservoir of it must be outside the metal case of the lamp.

The burner B is represented in fig. 22 in its cylindrical case, which is bent above, but must be gradually curved and not in a sharp knee. This bend directs the products of combustion into a chamber K, from which the passages for the deposition of the pigment proceed. The form of the upper part of the lamp-case is important. If it has an angular bend, the angle catches a lot of lampblack. This forms lumps which fall off, and partly get burnt in the flame and partly accumulate at the bottom of the lamp-case. A proper bend stops no lampblack, all of which goes to its appointed place.

The damper S is fitted into the lower part of the lamp-case, and must rotate easily. The wider the slots are left open by it, the more oxygen gets to the flame, and the faster the combustion proceeds. At one part of the lamp-case a well-fitting little door is made, to allow access to the wick, and there is also a window to permit the flame to be observed without opening the case. The screw R raises or lowers the wick. O is the reservoir for the lamp fuel, outside the case.

In the older types of lamp, the wick sucks up the fuel, and the attendant had always to take care to keep a supply of it in the reservoir. If this is neglected, the wick burns. This makes it suck up too much fuel, more than the lamp can burn. Most of the excess is simply distilled, and gives the lampblack the greasy smeary character above alluded to as making it unfit for further treatment. A careless and inattentive person can easily make this mistake, if he has a

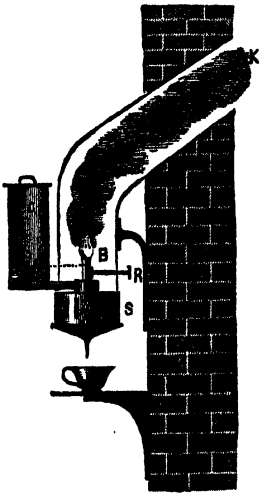


FIG. 22.

large number of lamps to look after. But from the reservoir shown in the figure the fuel does not flow out until its surface is below the line N. As soon as a little has been burnt, a little air enters the reservoir, which consequently supplies the lamp by gravitation until the opening N is again closed by the liquid. This make of lamp, however, only answers well with thin oils, and the greatest attention has to be paid to keeping the lamps clean.

All makes of lamp have disadvantages more or less. They have to be constantly cleaned, and there is always a waste of fuel when they are filled. There is a remedy for this, however, which consists in substituting for the separate fuel reservoir for each lamp one in common to a great number, and fitted to supply the lamps automatically. The attendant has then nothing to do but to supervise the air supply to each lamp, and to see that the mechanical arrangements for feeding the lamps with fuel are kept in good order.

With this automatic feed, all the burners must be in the same horizontal line, and must be immovably fixed. From each lamp a tube goes to a common tube running below the lamps. This latter opens into the free reservoir, and this is supplied from another larger one at a somewhat higher level. A cock in the tube between the two reservoirs is opened by a float in the lower one. If the level of the liquid in the latter sinks below a certain level the float opens the cock, so that the lower is kept supplied from the upper one up to a constant level. The float is so arranged, too, that the level of the liquid in the lower reservoir is just a little above that in the lamps. Thus there is just enough hydrostatic pressure to feed the lamps, and there is no difficulty in regulating the supply to the amount burnt. It is not easy to do so at first with a fuel of which one has had no experience, so as to burn all and waste none. To prevent any waste, the circular damper is made with a shallow concave bottom ending in a tube which opens above a small vessel, into which the funnel-shaped bottom of the damper directs any drippings.

In fig. 23, S is the damper and T the vessel to catch the waste. L is the tube bringing the fuel from the lower reservoir to the lamp by means of the common pipe H. A is the lower reservoir itself. When we use tar oils for lampblack making, and especially if we use thin light mineral oils, the tubes bringing the combustible to the

lamps may be small, but in burning thick liquids, such as fish oils, wider tubes must be used, as narrow ones would offer too great a resistance to the passage of the liquid.

It is well known that fats increase in fluidity with rise of temperature. Hence the stock reservoir should be in the same room with the lamps, so that in winter the liquid

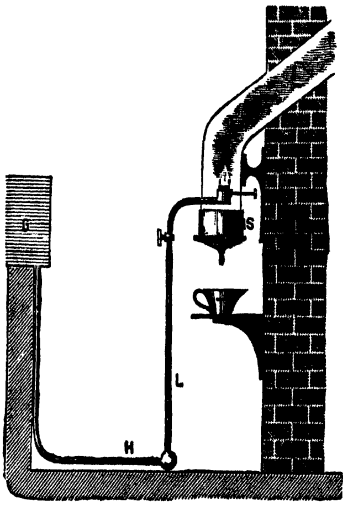


FIG. 23.

in it will be prevented by the heat from becoming too thick, and flowing too sluggishly through the pipes.

The reverse is, however, the case in using hydrocarbons from tar, brown coal, etc. In view of the low boiling points of these highly inflammable liquids special care is necessary in burning them. As they are always very fluid, even at low temperatures, it is advisable as a precaution against fire to keep the reservoir outside the lamp room, and to provide it with an air-tight cover pierced with only

a small hole to permit the necessary access of air for drawing off the liquid. Special care is necessary with such combustible and volatile bodies in regulating the supply to the lamps, or a large amount will be wasted by evaporation without being burnt.

The lampblack from the lamp is led into similar chambers to those already described, and removed from them as above stated.

Apparatus for Making Lampblack from Oil.

The patent apparatus (D.R.P. 9,426) represented in figs. 24 and 25 consists of a tube A closed at its lower end

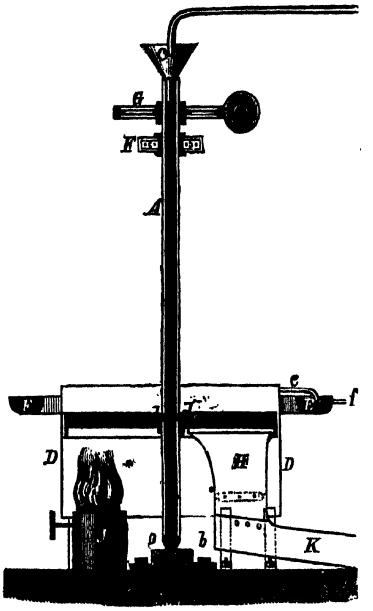


Fig. 24.

a, and supported by its point in the bearing B. This pipe is provided at *b* with a funnel *c*, which is used for pour-

ing in cooling water, which leaves the tube again through the holes *dd*. These holes are directly below a circular plate C of thin cast or wrought iron and is perpendicular to A which passes tightly through its centre. The plate is enclosed in the circular case, DD, of iron. From the top of this case the pipe *e* takes the cooling water into the circular gutter E, which is drained by the pipe I. A is supported above by passing through the bearing FF, and is rotated by the gearing GG. Near the bearing B is fixed a scraper H, the edge of which carries a strip of

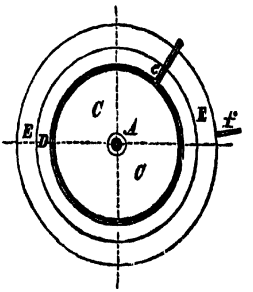


FIG. 25.

leather. Opposite the scraper is the lamp J with a wide flat wick.

The manufacture takes the following course: the apparatus having been set in slow rotation and cooling water having been set to flow gradually through the funnel *e* and out at *dd*, so as to keep the plate CC cold, the lamp J, previously filled with paraffin got by the distillation of brown coal, is lit at such a distance below the plate CC as is necessary to get, by the cooling effect of the plate on the flame, as much as possible of the carbon of the paraffin deposited on the plate in the form of lampblack. This lies light on the cold plate and also damp, because the coldness of the plate condenses the steam produced by the combustion.

The rotation of the plate is constantly offering a clean surface to the flame as the lampblack is perpetually being removed by the horizontal edge of the strip of leather on H, and sent by the gutter K into its destined receptacle.

Another apparatus on the same principle is shown in fig. 26.

The cylinder is a thin walled one of cast iron, with its exterior turned quite smooth. It is surrounded at a distance of a few cm. by an iron case. It turns in bearings on a

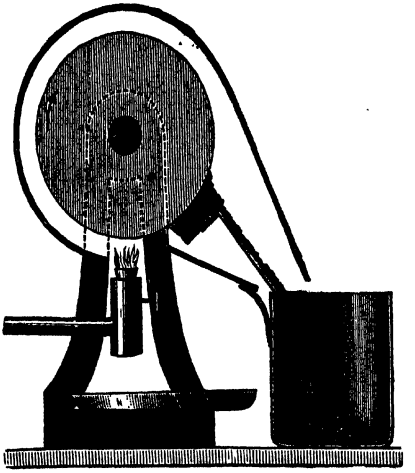


FIG. 26.

hollow axle, so that water can flow by gravitation through the inside of the cylinder. Below the cylinder are fixed the smoky lamps, in a row, and a soft brush extends over the whole length of the cylinder. This brushes off the lampblack over a sloping plate of iron into the receiver. The cylinder is kept in slow rotation by any suitable means.

The action of this apparatus is as follows. The lamps are so constructed as to produce a smoky flame and the lampblack they deposit on the outside of the cylinder is collected

from it by the brush. All the time the cylinder is kept cool by the water passing through it. The collected lampblack shows in consequence of this rapid cooling, which condenses other products, *viz.*, those of destructive distillation, a rather strong brown colour, and has to be made fit for use by subsequent ignition.

Dreyer's Apparatus.

The apparatus of R. Dreyer of Halle also depends on the fact that if a cold surface is brought into a luminous flame it becomes coated with a deposit of soot, as the temperature

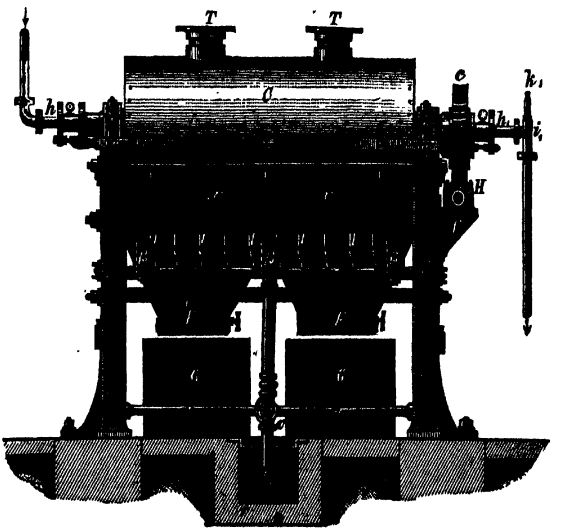


Fig. 27.

is brought below that necessary for the combustion of the carbon in the fuel, and is left behind in a finely divided free state. Fig. 27 is an elevation of the lower part of the apparatus; fig. 28 a longitudinal section; fig. 29 an end view, and fig. 30 a transverse section. Fig. 31 is a section

of the counterpoise ψ of the cylinder B and of the manhole π. Fig. 32 is a bird's-eye view of the bed plate of one side of the framing. Fig. 33 is an elevation of the upper part of the apparatus, and fig. 34 an end view of the same. Fig. 35 is a longitudinal section of the upper part, and fig.

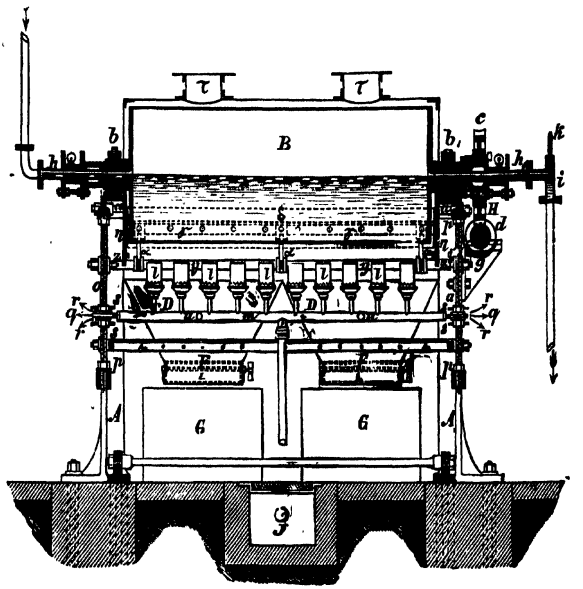


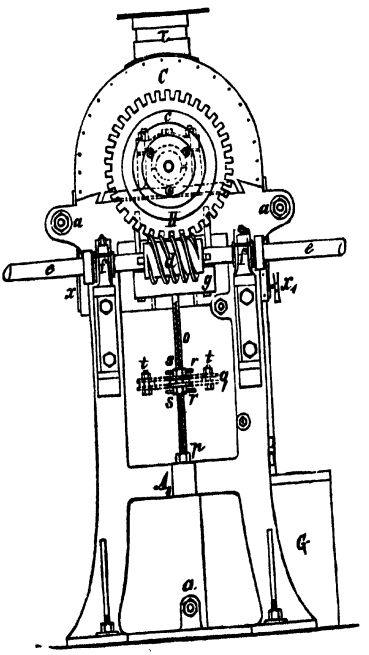
FIG. 28.

36 a transverse section of it. Fig. 37 is a bird's-eye view of it; fig. 38 a transverse section through the lampblack collectors *a*, and fig. 39 shows the cam *n*, and the lifting rod *o*. The principal parts are the frame AA, the cylinder B, the casing C, the lamp-guard D, the scraper E, the collecting funnels F, the gearing H and the aspirator K.

The frame consists of two side walls AA of cast iron

closely united by the screws *a*. The framing is bolted down to a suitable masonry foundation.

By means of the bearings *b* and b_1 the frame bears the cylinder B, with its outside turned smooth, and with hollow trunnions. The trunnion at b^1 has a hollow piece cast on to it to take the worm-wheel *c*, by which the motion of the



FIGS 29.

driving shaft *e* and the worm *d* the motive power is transmitted to the cylinder. The driving axle moves in the bearings *f* in the side-walls of the framing. To lessen cog friction a lubricator *g* is placed so that the worm touches the oil in it. Both the trunnion at *b* and the production of it at b^1 are provided with stuffing boxes, to receive water-tight the

tubes h and h^1 respectively; h^1 brings cold water in the direction of the arrow for cooling the interior of the cylinder, while the other carries off the warm water as it is replaced by fresh. So that the temperature of the outflow may be ascer-

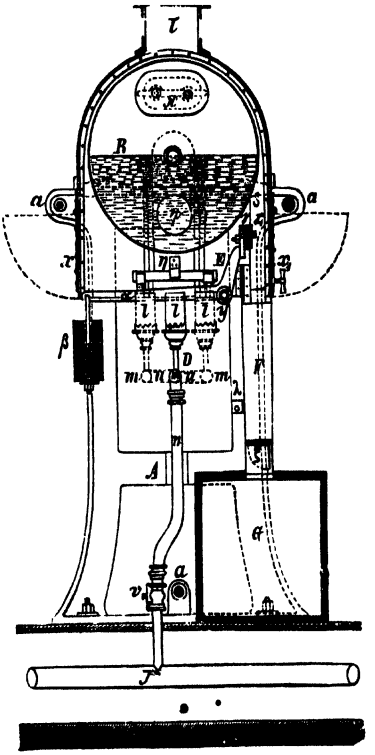


FIG. 30.

tained for the purpose of regulating the supply of cold water, and knee-tube i is inserted in the outflow tube, and in it is the thermometer R fitted into it by means of a cork. Under the cylinder B is the series of lamps D. The combustion

arrangement consists of the lamps *l*, the tube *m* distributing fuel to them, the indiarubber tube *n* and the mechanism attached to the side walls of the framing for regulating the distance between the lamps and the cylinder. This mechanism consists of upright screw threads at either end of the lamp series. The lamps and supply tubes are supported on nuts on these screws, so that their distance below the cylinder can be regulated by turning the nuts. The closed ends of the supply tubes have forks *g* at their closed ends by means of which they keep their position between the plates *r*. If more than one row of lamps is used the additional rows are sup-

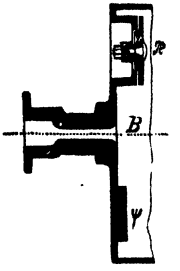


FIG. 31.

ported in their place by special screws *t*, as shown in fig. 29 in dotted lines. The various distribution tubes are then brought into communication by the cross-tubes *u*. These are of india-rubber to permit arranging the lamps under the cylinder, so as to save room and get a better distribution of the lampblack on the cylinder. In a channel under the apparatus is the main tube J which brings the combustible to the lamps. The supply can be regulated by the cock *v*, and J is in flexible communication with the separate supply tubes by means of the india-rubber tube *n*. At a distance from the cylinder B of a few cm. is the iron casing C, which rests by means of the handles *w* on the side walls of the frame. The lower part of this casing consists of two lids *x* and *x*. One of these

is to facilitate access to the lamps, the other to the stripper E. The stripper E consists of the axle *y*, which is kept fixed by screws and nuts to projections in the side walls of the framing; the three knee levers *a* with counterpoises B, the guides *yy*, with the elastic steel plate *d* between them which scrapes the lampblack from the cylinder. The nearer the lamps can be got to this steel plate the better, as the lampblack is delivered in a drier state. The steel plate is fixed to the rails *yy* by screws which work in slots so as to permit the edge of the scraper to be brought nearer to the cylinder as it wears. To fill up the slits in the end of the casing where the trunnions of the cylinder pass, various pieces *y* are inserted, which are kept in place by grooves and bolts. On

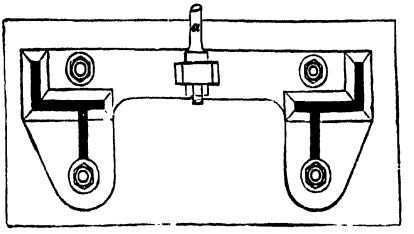


FIG. 32.

the casing C two projections are made which support the aspirator K with the draw-off pipes. A manhole π with a cover is provided to enable the inside of the cylinder to be cleaned. The manhole cover is balanced by the counterweight ψ. The funnels for collecting the lampblack are at one side of the casing, and are carried by the angle iron ψ, which is fixed to the side walls of the framing. In order that the collecting vessels G can be changed for emptying purposes without allowing any lampblack to fall on the ground, a door with a handle is attached to each funnel and can be secured to a bolt.

The upper part of the apparatus shown in figs. 33 to 39 inclusive consists of the aspirator K, and draw-off pipes

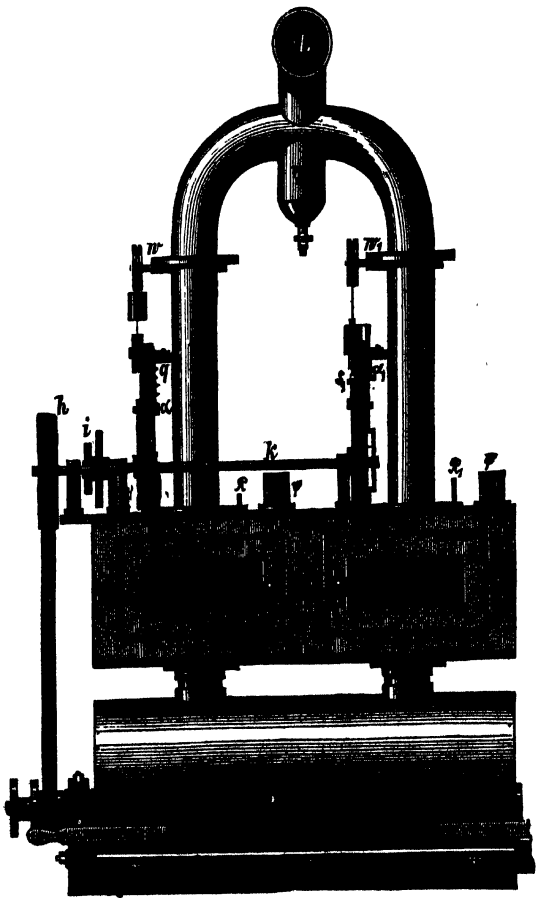


FIG. 33.

communicating with an exhaustor. The object of this arrangement is to prevent the so-called sweating of the workroom,

and to ventilate it for the better health of the operatives, as well as to catch any lampblack which does not settle on the

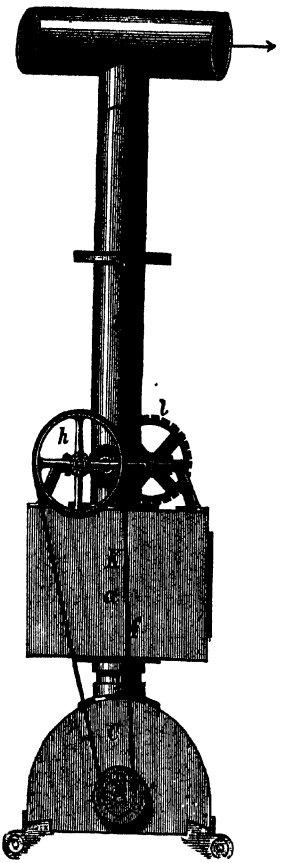


FIG. 34.

cylinder, and save waste thereby, and at the same time to prevent the deposition of such lampblack in wrong places. With the intentionally imperfect combustion of the fuel not

only lampblack but water is produced, which becomes steam through the heat of the cylinder. This steam mixed with air out of the factory, and kept in by the casing, is drawn by the exhaustor through the aspirator K, where it is freed from any particles of lampblack, and sent out as warm damp air into

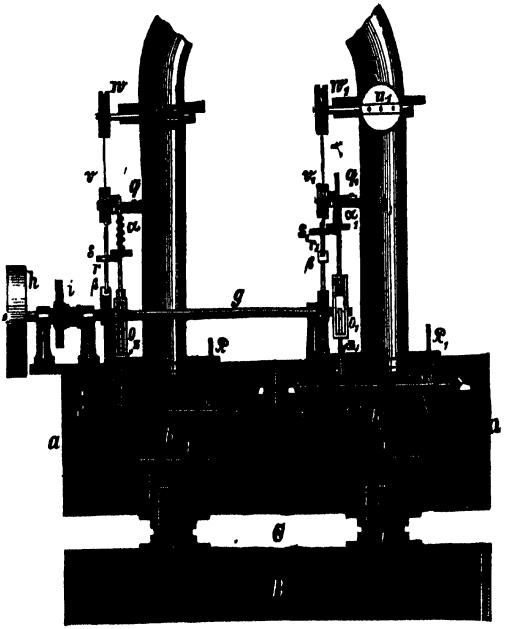


FIG. 35.

the outer world. To this aspirator belongs the wooden box *aa*. This is divided by a partition and lined with tin-plate and felt to keep the inside warm. Each of the two compartments of this box is accessible by a little door and contains a lampblack-catcher, consisting of a saw-shaped piece of iron covered with flannel. To make these flannel walls *c* and the wooden frame *d* are employed. The wooden frame is supported by the edgings *e*. To prevent the filters from being

choked by accumulations of lampblack, an automatic arrangement for tapping them is attached to the cover of the wooden box. The necessary motive power for this is brought by a belt F from the cylinder axle to the pulley h on the axle g. By means of a suitable gearing the axle k is driven from the

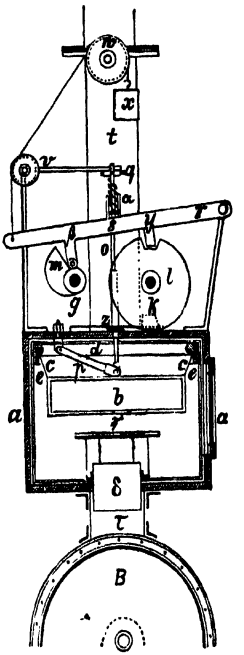


FIG. 36.

axle g, but at a much slower rate. On the axle k are the two discs 1 and 1'. In the circumferences of each of these is a gap, the two being exactly opposite each other. On the axle g sit opposite the pulleys m and m^1, which have near them and on the same axle the pulleys n and n_1 each with a corresponding number of cams which engage in the correspondingly

slotted lifters o and o^1. These lifters are at their lower ends hinged to the flannel filters, partly directly and partly through the intermediate levers p and p^1. The upper ends of the lifters are guided in the slots q and q^1. For the better regulation of the movements of the flannel filters, the parts of them by which they are connected with the levers which are not directly connected with the slotted lifters are provided with guide pieces π and π_1. Over the pulleys ll, d, m, m_1, are the levers r and r_1 supported at one end. These levers, by means of rods s and s_1 attached to the slotted lifters, permit the flannels to be raised and keep them in that position.

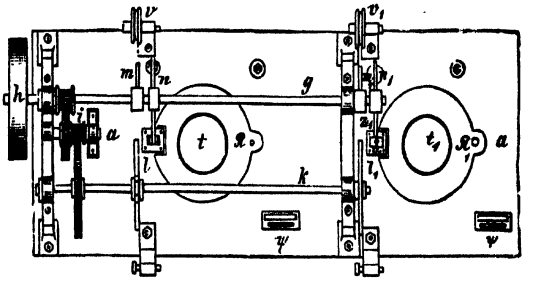


FIG. 37.

Each of the draw-off pipes t and t_1 is provided at its upper end with a valve (u and u_1). These valves are made to shut the draw-off pipes by means of chains, passing over the small rollers v and v_1, the levels r and r_1, and the pulleys w and w_1. The valves are opened by the counterweights x and x_1. When the pulley l and the cam m have arrived at the positions shown in fig. 36 the projection y on the lever r lies in the notch of the pulley l, and closes partly by its own weight and partly by the help of that of the descending flannel filter, the valve u of the draw-off pipes, at the same time raising the counterweight which opens the valve. As soon as this has taken place, the pulley n comes into play. By the cams the slotted lifter of the flannel filter is lifted up and let drop

repeatedly. At the same time the lifters strike the metal plates z and z_1 and so knock the lampblack off the filters.

To make the execution of these movements exact, the spiral springs a_1 and a_2 are also added. After the flannel filter has again come to rest, the cam m comes into action once more, by raising the roller-provided projection β of the lever r, which in its turn raises the slotted lifter o. Hence the slotting of the lifter comes into such a position that the cam n can no longer act. The cam l has been all this time approaching with its notch the projection ϕ, so far as to keep the lever r, the lifter d, and the flannel filter b in their

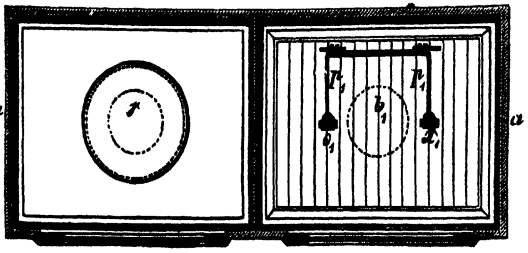


FIG. 38.

nighest positions, and its outer edge comes under the projection ϕ. To further ensure proper working of the cam l, the cam n has a corresponding circumference. At the same time the counterpoise x comes into play, and opens the draw-off pipe t by means of the throttle valve u.

To prevent the lampblack knocked off the filters from falling back on to the cylinder B, the covers y, y_1 and the projections d and d_1 are added. The feet under these covers leave so much free opening that the warm moist air from the casing can get into the inside of the wooden box. The use of two lampblack-catchers produces a permanent ventilation of the workroom, and at the same time an uninterrupted removal of the steam, for as the notches in the cams l and l_1 are directly opposite each other, one compartment of the box

at least is always ventilating while the way through the other is closed by the throttle-valve so that there is no air current through it.

In order that it may be seen whether the flannel filters are acting properly, a vacuum gauge ψ is fitted on the cover of each compartment of the wooden box. By proper choice of the diameter of the belt pulley and the relative numbers of teeth in the gearing wheels, the shaking off of the lampblack

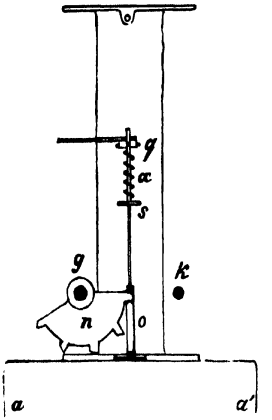


FIG. 39.

from the filters may be arranged to take place at any desired intervals. The two draw-off pipes t and t_1 are connected with the exhauster, and if more than one of the pieces of apparatus described is used the draw-off pipes of each are connected by elbows with a common main L which proceeds to the exhauster. A cock is provided for drawing off condense water from this main.

TIGHE'S PROCESS.

In the preparation of lampblack according to the American patent of Tighe of Pittsburg, the vapour of hydrocarbons is

exposed to a high temperature in a retort, so that no combustion, but dissociation, ensues. On cooling the products lampblack is deposited. It may be questioned whether this process will give carbon finely enough divided in view of the graphite-like nature of carbon deposited in glass retorts.

Chemical Preparation of Lampblack.

With whatever care the manufacture of lampblack may be carried out, we never get a perfectly black product, because the carbon is invariably accompanied by a greater or less quantity of the products of distillation, partly solid and partly liquid. The effect of the presence of these bodies is that the lampblack is more or less of a brownish shade, which becomes best seen when the lampblack is spread out on paper. When the layer is of a certain thickness it will be clear that the colour is not black, but an impure brown. If we analyse such lampblack just as it comes from the flues, we shall see that various chemical solvents dissolve ingredients of the lampblack, sometimes in large quantities. It is, in fact, possible by proper chemical treatment to remove the foreign bodies from the carbon almost entirely, so that a substance is left consisting practically of pure carbon. This rightly purified product can be got by boiling the lampblack repeatedly in strong caustic soda lye until the lye remains colourless. When caustic soda has dissolved out all it can, but not before, the residue is boiled with *aqua regia* till that has dissolved all it can. When the *aqua regia* too remains colourless, every trace of acid is washed away with water, and the lampblack is then finally dried.

As a result of this treatment the lampblack becomes an extremely soft powder of the purest black hue known, and consists of chemically pure carbon in the amorphous state. When heated on platinum foil, it burns to pure carbonic acid, without the production of either smoke or smell. In practice, the purification of the lampblack is not carried quite so far as

to get chemically pure carbon. If this were done, the yield would be made too small, without sensibly improving the product as an article of commerce. The object of the manufacturer is gained as soon as his lampblack is no longer brown but black.

We can use the solvent action of caustic soda lye to get rid of the brown bodies which are mixed with the raw product. For this purpose we boil the lampblack several times in iron vessels with the strong lye. It is, however, unnecessary to keep on until the lye remains colourless; we may stop when it has a pale brown colour only. Even at this stage, the lampblack has no perceptible tinge of brown and appears as a velvety black and extremely soft powder, of very great covering power. Even although caustic lye is now fairly cheap, this method of purifying lampblack must be regarded as a rather costly one, because it requires much labour. Hence it is only employed in making the finest lampblack for special purposes.

Calcining Lampblack.

As already mentioned, the substances which make lampblack brown are products of dry distillation and are therefore volatile. The lampblack can hence be purified from them by heating it without contact of air. The temperature required to get rid of them entirely is somewhat high and it is necessary to raise the pigment to a bright red heat to be sure of success. If the heating is too rapidly done or the temperature is too high, the lampblack suffers a change which injures its quality, as the flaky form of the pigment is lost, and it takes the shape of grains which require much longer rubbing up with boiled oil to produce a uniform mass. The flaky lampblack on the other hand mixes with the oil easily and rapidly.

For the ignition of lampblack boxes of sheet iron are used, painted outside to protect the metal from the fill. This

painting is best done with an ordinary plaster of loam and hair. The loam is stirred up with water to a very thin paste, which is painted uniformly over the outside of the iron box with a brush, repeating the application several times, but never applying another coat till the last is dry. When this is finished, several more coats are applied, the loam being this time mixed with chopped tow or cowhair. This is repeated until the total thickness of the coating is several mm. Such a coating, carefully laid on sticks very close, enables the boxes to be used for a very long time, while unprotected ones are quickly burnt through.

Very special care must be used with the boxes. Their bottoms should be coated with loam, and the covers must fit accurately and the join must be caulked with loam while the box is in use. The lampblack must be rammed into the boxes to a solid mass. A very small hole is made in the cover to allow of the escape of the volatile bodies. When the boxes are placed in the furnace, they are gradually heated, applying the heat first at one end.

The temperature is gradually raised, and extended over the rest of the box. Finally a bright red heat is reached at which the box is kept for half an hour. This treatment drives off the volatile matters almost entirely and gives the lampblack its proper black colour. As above stated the greatest care must be taken to protect the lampblack from the air while it is red hot, as it is very combustible. The small opening in the cover for letting out the volatile bodies must be the only orifice of any kind. Even a crevice invisible to the naked eye will let in quite enough air as the box cools to produce a very noticeable loss of lampblack by combustion.

To prevent this loss altogether the cooling of the boxes must be attended by special precautions. When the boxes are withdrawn from the fire with tongs and left to cool, air can get in at the small hole in the lid; if, however, a red-

hot coal is laid on this hole the oxygen of the air is converted into carbonic acid as it enters, and hence any burning of the lampblack is rendered impossible, as no oxygen but carbonic acid only comes into contact with it. As soon as all the boxes are taken out of the furnace, they are exposed to a free current of air to cool them as quickly as possible.

As finely divided carbon burns at a temperature much below redness, the boxes must not be opened till their contents are quite cold. An attempt to empty them while hot might cause the whole contents to burn.

To get lampblack of great fineness and depth of black, a single calcination is insufficient. The procedure must be repeated as often as five times, and for specially fine kinds even oftener.

CHAPTER XIV.

SUBSTITUTES FOR LAMPBLACK.

The unavoidably complicated nature of lampblack manufacture, and the want of uniformity of the products delivered by manufacturers, have necessarily created attempts to find substitutes for lampblack. Whether these substitutes have justified themselves in practice has not become known, but I think they might at all events be used for common pigments, so long as their specific gravity is not too great, and there is no danger of their separating out from the mixed paint. Among these substitutes are blacks from tar, and tannin-black from leather-cuttings, the production of which will here be fully described.

Black from Tar.

A factory recently erected for the manufacture of black pigment from tar, and which sends its product mostly to England, has six boilers, heated by tar, which supply steam for an 8 h.p. engine. The boilers are arranged so as to afford free access to each of them. Each boiler is 4 metres long and ·65 metre in diameter. Each is carried on brickwork by two bearers, and both open into a common steam chest above them. The tar is brought in casks by a small railway to the front of each boiler, where there is a container holding 2 caskfuls, and emptied into it. Behind each boiler is a chamber, in which the black smoke developed from the burning tar, which has been gradually cooled by passing under the boiler, deposits the lampblack on iron plates disposed horizontally and vertically in various parts of the

chamber. The lightest black is deposited in the upper parts of the chamber which have not to be emptied so often as the middle and lower parts, which are relieved of their contents after the combustion of each charge of tar, *i.e.*, after the combustion of the two caskfuls from the container in front of the boiler. Three boilers are fired

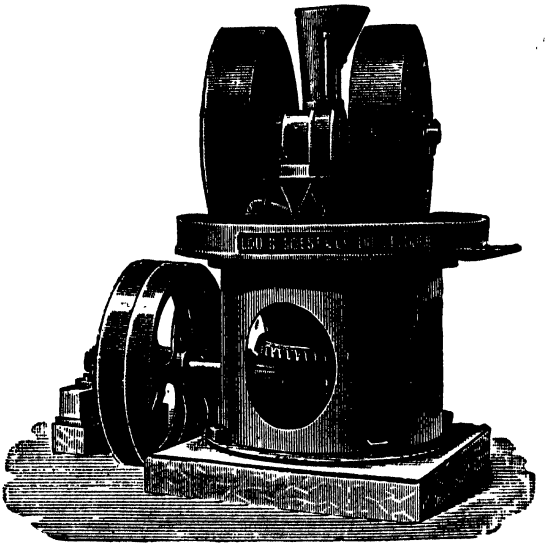


FIG. 40.

at a time, so that steam is kept up by one trio while the charge of lampblack is being drawn from the other. The residue on the grates is fine coke. The chambers are covered with iron plates, and rise to a height of 5 metres, being 1 metre above the roof, so that the upper part can be emptied from without by means of an iron ladder, while the lower divisions of the chambers are emptied from inside the boiler house by means of iron doors in them. The largest part of the black settles in the lower compart-

ments as above stated. The lampblack from these is for the most part mixed with peat, finely ground in a pug-mill, and is then packed in barrels. A small part of it, however, is sent away without any admixture of peat. The 8-horse engine provides the power for driving the pug-mill, the peat-preparing apparatus, the mixing plant, as well as for a packing machine, a cask-making machine, etc. The cost of installing a factory, such as above described, with the six boilers is from M.8,000 to M.9,000.

Preparation of Tannin Black.

The raw material for this product is waste leather of every kind, old leather and leather articles, and also animal waste containing gelatine, and tanniferous products of all sorts, barks, fruits, leaves and roots. These substances are dissolved with or without steam in two different operations.

1. Five hundred kilos. of the mass is mixed with about 1,600 litres of water in a vessel, and the whole is then heated by steam for a few hours without, however, being allowed to boil. This first decoction is then drawn off, and another lot of water is added with about 25 kilos. of caustic soda or the equivalent quantity of carbonate. The whole is then boiled for a few hours, and the decoction is added to the first one, to which have been added in the meantime about 4 kilos. of ferrous sulphate or the equivalent amount of chloride, acetate, or sulphide, to precipitate the gallotannic acid. This should be down by the time the second decoction is ready. After the second decoction has been run off, 14 kilos. more of ferrous sulphate or an equivalent amount of one of the above alternatives is added, with a little alum to complete the precipitation. After careful stirring the mass is left to stand for a time and then pumped through a filter-press to free it from water. The black is got from the filter-press in solid cakes. To prevent any liability on the part of the black to get mouldy, about 16 litres of heavy tar

oil are added to each of the two decoctions. The oil owes its preservative power to the presence in it of creosote and carbolic acid.

2. We treat 500 kilos. of leather exactly as in No. 1, except that 15 kilos. of caustic soda (or its equivalent of carbonate) is used for the first decoction and 20 kilos. instead of 25 kilos. for the second decoction. The same amounts of iron salts, of water, and of tar oil are used as given above, and the whole process is identical with the exception mentioned.

If the black is to be used for printers' ink, a little cyanide of potassium or logwood extract or decoction is mixed with the precipitate, so as to give it a blue or violet tinge.

After leaving the filter-press, the mass is washed with steam to free it from adhering salts. The quantities given above can be altered without affecting the principle of the invention.

For printers' ink the black is dried till it has lost half its weight, and will then make with boiled oil a mixture in any proportion which may be desired. To make oil paints we proceed in similar fashion with black and drying oil.

An improved process is described as follows. The leather cuttings are mixed with a suitable quantity of iron-salt, preferably the chloride, corresponding to the amount of tannin in the leather. On the average 500 kilos. of cuttings require 30 kilos. of solid chloride. The mass is then covered with water and boiled up with direct steam. The boiling lasts five or six hours, until the whole mass has become black. The boiling can also be done by a steam jacket or a naked fire. The mass is then thoroughly washed with hot water or steam, the acid washings are neutralised with powdered iron ore or scrap iron, and can then be used instead of part of the next lot of chloride of iron.

The solid residue is dried and ground fine. It can be used for making printers' ink instead of lampblack.

CHAPTER XV.

MACHINERY FOR GRINDING AND RUBBING UP PIGMENTS.

Although nearly all the pigments which the maker of oil-paints and printing inks uses are delivered to him in the finest powder, it may happen that he has to grind a lump pigment or that the pigment he has bought, although it has been ground, has not been ground fine enough for his purpose. Experience has taught us that pigments when in the form of the finest possible powder can not only be worked up the most quickly and easily, but give the best products, as they are much more ready to mix uniformly with the vehicle. When rubbing up thick colours, *i.e.*, with a small amount of vehicle, care must be taken that the machinery is not clogged, and so perhaps stopped altogether.

Earth-colours, such as the ochres, ball when stocked damp or have become damp during carriage, and when dried again form hard lumps which must be ground before being mixed with any vehicle.

The most simple apparatus for grinding such lumps is a pug-mill, which consists of two flat circular stones, which move in a metal or wooden pan with a bottom of metal or stone, by means of toothed gearing, and crush the lumps by their weight, converting them into a powder more or less fine.

Bonner Ball-mill.

The ball-mill of the Bonner Bergwerks und Huttenvereins consists of a casing having the form of a cylinder with ends

consisting of segments of spheres. This includes a loose ball of only slightly less diameter than the cylinder. The apparatus is represented in fig. 41. The casing is made of cast iron or steel, and should be in as few pieces as possible. The one in the figure consists of four segments B and two side walls C C, which are kept together by bolts *c*. As a result of this very simple construction it is possible to replace a damaged or worn one with great quickness and ease.

The side walls C C are pierced by the hollow trunnions $C\ C^2$, whose bearings are on the framing G G, and on which

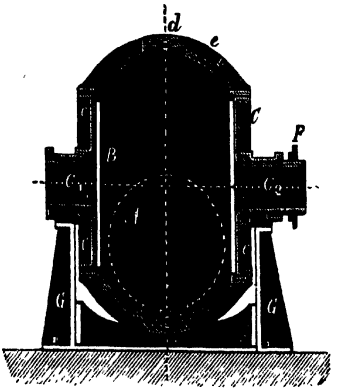


FIG. 41.

the casing rotates. The axles are hollow, so that the material to be ground and the products of the grinding can be passed through them. The mill is filled through C^1, and an exhauster sucks the ground stuff out through C^2. The grinding ball is of iron or steel and weighs from 1,500 to 3,000 kilos. according to the nature of the material to be ground. As above stated the ball has a little side-play between the sides of the cylinder. This arrangement has a great advantage over the old-fashioned contrivance of a stone-roller running in a casing, as it never

causes clogging, which so frequently occurs with the roller. Most of the grinding is done by the sideway play of the ball. The casing is best turned direct by putting a belt round it, as shown in fig. 42. It is of great advantage in increasing the work done by the machine to have niches *a* along the path of the ball. These get filled with partly ground stuff which is constantly emptied out of them by the rotation of the casing and thrown back on to the ball again. The niches thus serve to lift up the material and distribute it. The running of the ball in its path and its side-play make the action analogous to that of rollers without the complexity and unreliability of the roller-mill. The ball should not have too much play, as if it has the grinding will be slower.

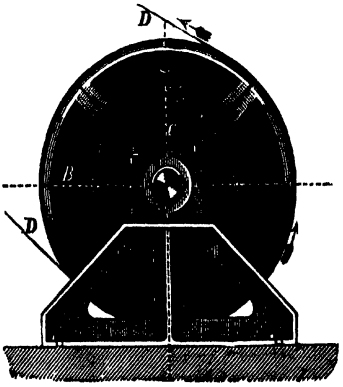


FIG. 42.

When the grinding is finished the product is removed by the exhauster. It is a good plan to insert between the mill and the exhauster a series of chambers in which the product will sort itself, the finest being deposited in that farthest from the mill, and the coarsest in that farthest from the exhauster.

Another very excellent machine for grinding pigments is

Glaser's Disintegrator.

The action of this new form of mill, shown in fig. 43, depends upon the rotation of a disc armed with projecting

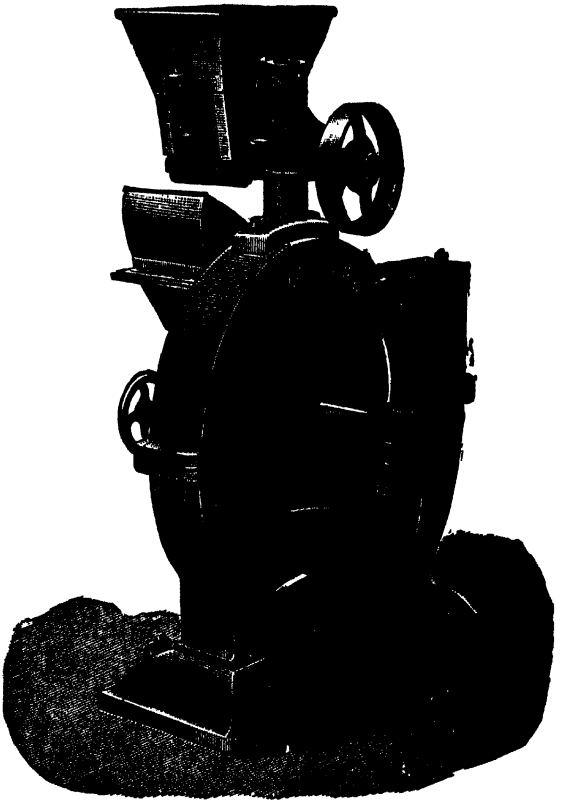


Fig. 43.

beaters, which knock the material against the sides of the casing in which the disc runs till it is broken up small enough to fall through a sieve out of the mill.

This mill has great advantages over other similar systems.

It is built much more simply and solidly, has only one driving belt, is easier and quicker to clean, wears out less and requires no special foundation. The characteristic action of this mill explains its extremely large output for a comparatively small amount of wear and consumption of energy. The new mill requires no sharpening, and worn parts can be cheaply and easily replaced. In grinding wet, sticky, or resinous material, it is very rare for the mill to choke, and if it does it can be cleared in a few minutes. It is also an excellent apparatus for intimately mixing bodies together.

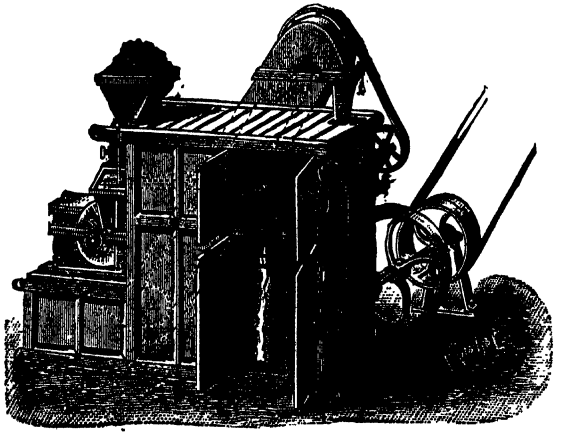


FIG. 44.

The machine can be fed with pieces the size of a hazelnut or the fist, according to the size of the mill and the character of the stuff to be ground. To bring the material into small enough pieces to go in the mill, other apparatus has to be used when necessary. A preliminary breaking apparatus which will take pieces twice the size of a fist may be had attached to the mill. A hand wheel permits the regulation and the clearance of the disc carrying the beaters from the inside of the case, so that the material can be ground coarser

or finer at will, a correspondingly sized sieve being, of course, also used.

Wherever, as in colour grinding, a very finely powdered and absolutely uniform product is demanded, a sieve is essential, and various well-constructed sifters are to be had. In Glaser's mill the regular feeding is provided for by elevators which raise the material to the necessary height, and then carry it horizontally into the mill, such as Archimedean

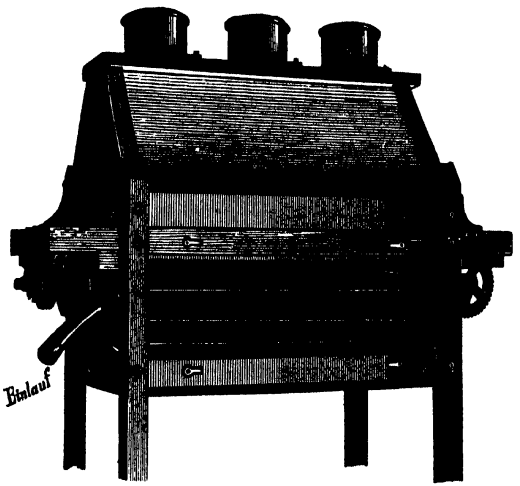


FIG. 45.

screws, etc. In order to get the proper speed, complete series of belt pulleys should be provided. The mills for a daily output of 400, 1,500, 4,000, 8,000 and 15,000 kilos. for medium, heavy and hard material, and for a medium fineness of grinding at from 120 to 1,200 gulden Austrian currency require, with a speed of 4,000, 3,000, 2,000, 1,000 and 300 revolutions, a power of ¾, 2, 4, 6 and 10 h.p.

A very pretty combined mill and sifting apparatus by the same firm is represented in fig. 44. It consists of a mill,

elevator, sieve, dust-chamber, a feeding hopper, gearing, etc. It can be put down anywhere convenient without special fixing, and started at once by connecting it with a belt to the driving power. No attention is required except to keep the hopper supplied, and to remove the stuff as it is ground. To remove bits of iron which are common in grist in the shape of nails, etc., magnetic apparatus is provided.

The fine powder got with these various mills is not in all

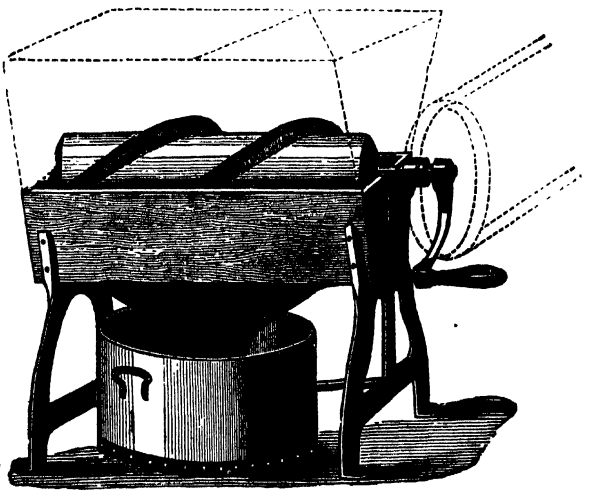


Fig. 46.

cases fit for immediate use, but must be sieved for sorting it into various degrees of fineness. As this is impossible with hand sieves, partly on account of the large quantities to be dealt with and partly because the dust would be injurious to the health of the sifter, various kinds of sifting and winnowing machines of known construction are employed.

Centrifugal Sifting and Winnowing Machine.

The centrifugal sifting and winnowing machine represented in fig. 45, by Zemsch of Wiesbaden, is used when the sifting

of similar substances is to be done, or some amount of admixture in the sifting of the substance with others previously sifted is unimportant, as the drum inside the case is awkward to clean. Quick rotation is given to the sifting cylinder, in which beaters are moved by gearing, as soon as the rotation begins. The grist enters through a safety basket to catch stones, nails, etc., into one end of the machine. Dust cannot fly about and the finest brass or silk gauze can be used for the sifting.

Sieving and Mixing Machine.

The machine shown in fig. 46 serves for simultaneous sifting and mixing. It is the only existing arrangement whereby the whole of the bolting cloth can be taken out quickly and easily if it is desired to substitute a different mesh. The brush roller, set with the best stiff bristles, rotates in a semi-cylindrical sieve, and can be approached thereto as the brushes wear. It is enclosed hermetically so that no dust can fly about. Any lumps in the grist are completely destroyed by the rotating cylinder. The product of the machine falls into a receptacle below, while anything too coarse to go through the machine leaves it at one end. The sieves are made of strong iron or brass wire, and fixed into their place by soldering. They are very durable. A corrugated iron half cylinder is substituted for the sieve for mixing powders with liquids. The arrangement of the brushes, like an Archimedean screw, provides a horizontal as well as a rotatory motion, which makes the mixing more complete and more rapid.

CHAPTER XVI.

MECHANICAL CONTRIVANCES FOR MIXING VEHICLES WITH PIGMENTS.

When large quantities of pigment have to be dealt with mixing them by hand is a toilsome and time-wasting process, and must be replaced by mechanical mixers. Such contrivances are the more essential when the paint has to be mixed very stiff, *i.e.*, with very little vehicle, or when, as in printing inks, the vehicle itself is tough and the pigment (like lampblack for example) is very light, in which case the amalgamation of the two is very difficult. In fact it is practically impossible to effect it at all by hand, except in extremely small quantities. For thin colours containing much vehicle the machines may be dispensed with, but for thick and tough mixtures they are indispensable.

Quack's Machine.

A very simple apparatus for the purpose is the mixing and kneading machine of E. Quack.

Figs. 47 and 48 show the machine in vertical section and in elevation respectively. In the cylinder with smooth walls turn two blades overlapping as shown. They turn in opposite directions, and work the contents of the machine into a perfect mixture in a very short time and with a less expenditure of power than any other machine. The work goes on with mechanical accuracy to its termination. The particles under treatment are driven about until the whole mass has been worked through. The rotating blades scrape each other and also the walls of the cylinder, so that nothing can escape them;

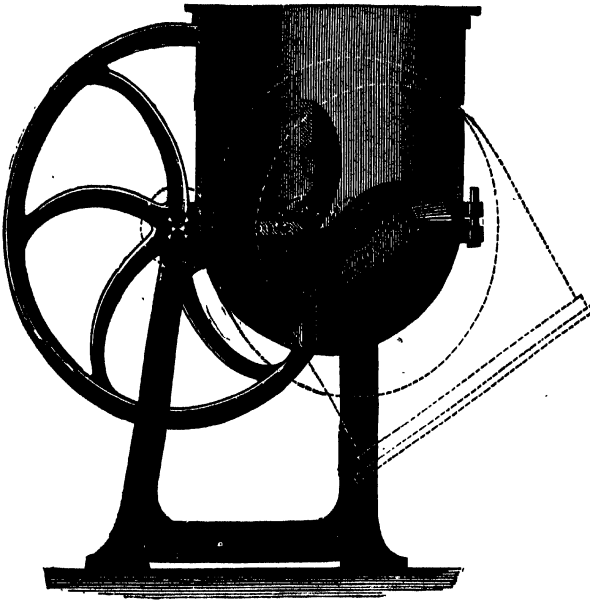


FIG. 47.

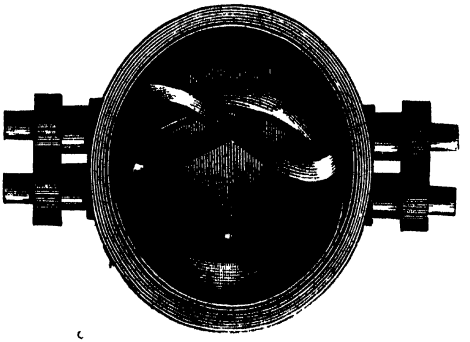


FIG. 48.

The machine is emptied by just tilting it, the blades being kept going on all the time to prevent anything from remain-

ing sticking to the walls of the cylinder. When the machine wants cleaning it can be at once taken to pieces by loosening a few wedges.

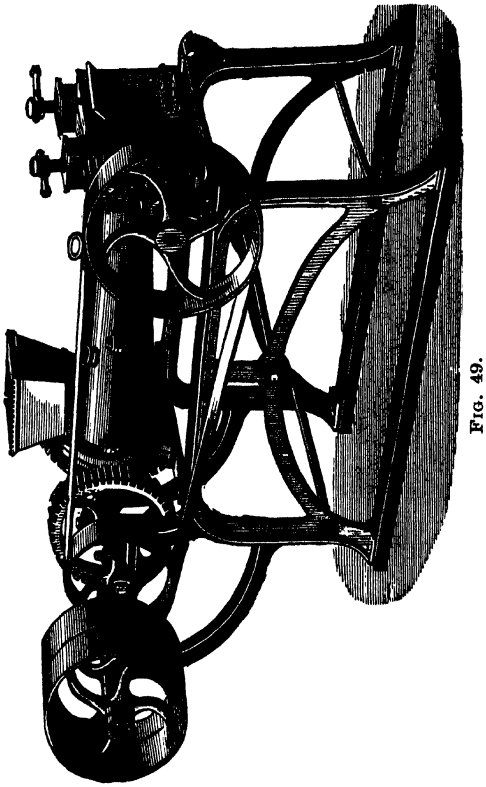


Fig. 49.

Werner and Pfleiderer's Machine.

The kneading and mixing machine of Werner and Pfleiderer of Cannstatt has the most simple principle imaginable (see figs. 50*a*, 50*b*), and it is said to have achieved results hitherto impossible. The machines are made in all sorts of sizes

from a capacity of ½ up to 1,400 kilos. The charge that can be worked up at one time depends not only on the sp. gr. of the substance, but to a large extent on its consistency and other properties. In most cases a machine of the stronger class is well suited by its shovel form and general construction to do the work of a small machine on occasion, but the

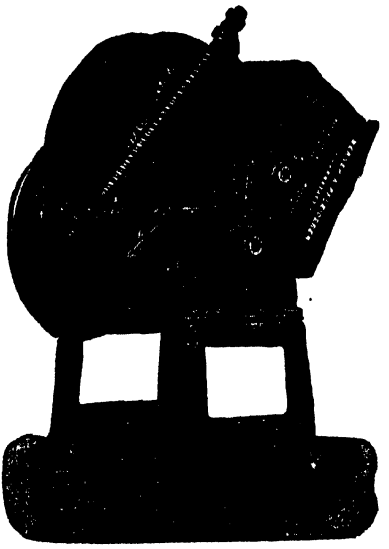


FIG. 50*a*.

use the machine is to be put to, *e.g.*, whether it is for oil-paint or for printers' ink, should be specified on ordering.

In working the kneading knives rotate in opposite directions inside the case. To save time and increase the action the motion must be reversed from time to time. The machine works best when not too full for the lively and characteristic movements of the mass to be observed. With dry materials even when the blades are entirely covered these movements can be seen. The machine is tipped up to empty it. Some

of the machines can be readily taken to pieces to be cleaned the trough and the blades separately.

Lehmann's Machine.

J. M. Lehmann of Dresden Löbtau mixing machine for pigments is represented in figs. 49 and 51. The machine represented in fig. 51 consists as will be seen of a strong iron

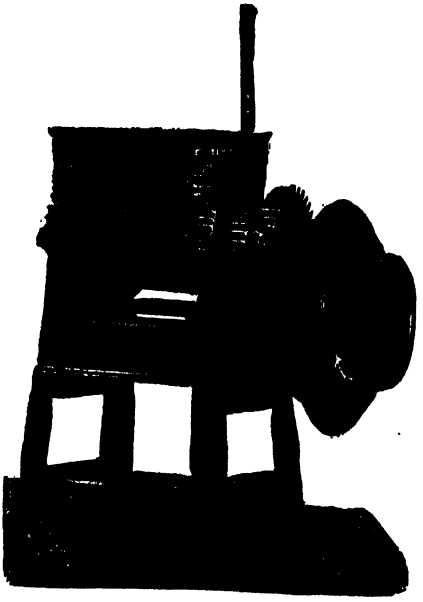


Fig. 50½.

stand bearing a cylindrical trough, which can be rotated on its longest axis. It contains a mixing arrangement consisting of segment-shaped blades which, when the trough is rotated, produce a thorough amalgamation of the contents of the trough, whether dry powder, boiled oil, or mixtures of oil and pigment.

The machine is made in two sizes for 200 and for 40 kilos. of pigment, and costs M.500 and M.400 respectively.

All these machines mix together oil and pigment in a complete manner, but do not make the pigment any finer-grained. They do not give the ointment-like consistency characteristic

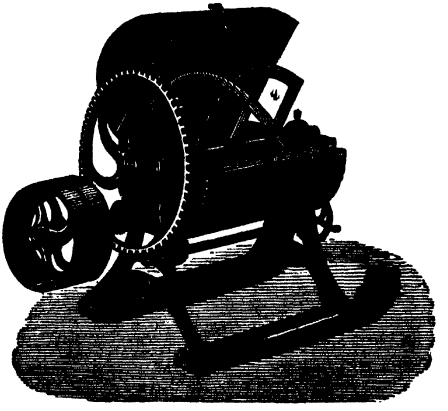


FIG. 51.

of a good oil paint, but a lumpy mass which has to be rubbed down with the hand or on a stone by means of a muller.

To get the ointment-like consistency, further treatment is required, which combines mixing with crushing. For very small quantities a stone and muller suffice, but special machinery called paint mills is needed for large quantities.

CHAPTER XVII.

PAINT MILLS.

These machines may be classified as follows:—

1. Those which work by taking the material between two slanting corrugated surfaces, one of which is stationary while the other rotates.

2. Those which take it between two flat-ribbed surfaces, which both move eccentrically but in opposite directions.

3. Those which take it through a system of from two to four rotating rollers of steel, bronze, stone, or porcelain.

The first class is the one most used. The machines belonging to it are cheap and are made in all sizes, and several of them are to be found in every paint factory.

Their simple construction is shown in fig. 52. They are entirely of iron, except the rubbing surfaces which are of bell or gun metal. The mixed colour is put into the funnel T, the grinding disc M is pressed more or less on to the funnel T by means of the set screw S, according to whether the scraper P is to deliver a finer or a coarser colour. The grinding disc is provided inside with notches which run towards the conical point in the centre of it. The interior of the funnel is also grooved. As these grooves wear they must be filed out again, because on them depends the fineness of the colour. The machine stands on a tripod. In an improved form specially introduced by the Brockhaus firm for printing inks there is a massive stand, and the funnel is more than twice as deep.

The chief drawback of this machine is that its output is small, as the colour stays in it long after it is finished. The

finer the colour has to be rubbed down, the more this inconvenience makes itself felt, and in fact when very thick colours are being rubbed very fine hardly anything will come out of the machine. Schlager of Ybbs has improved the machine by taking away the stand, and putting the grinding disc and funnel on a common vertical axis. The funnel is also closed,

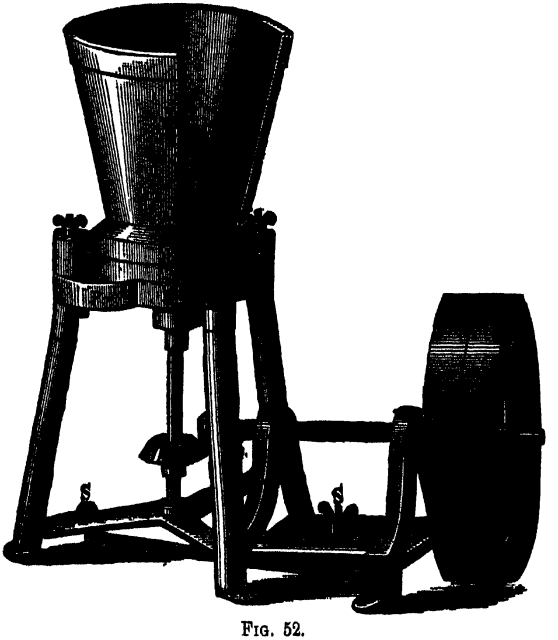


FIG. 52.

and air pressure is exerted upon the pigment within it by means of a pump. This pressure drives the finished colour out of the machine. The pump is geared with the machine so that both are set in motion together, and very little power is required. Many tests have shown that these alterations have not only greatly increased the output of the machine, but that the machines can be made very much lighter.

Plate Machines.

The plate machines belong to the second class, and give an excellent output. They rub extraordinarily fine and last for years without repairs on account of their very solid construction. The machine consists of a massive cast-iron

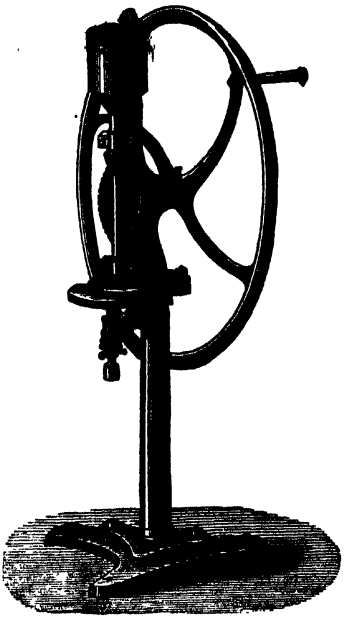


Fig. 53.

stand, two plates, the spindle or axle, which is closely united to the funnel, and has a strong spiral spring inside of iron wire, the funnel to receive the colour, and the set-screw under the lower plate. When the machine is to be started, we put the plates close together by means of the set screw, fill the funnel with paint, release the plates a little and set the gearing in motion. The upper plate and the funnel then

rotate with a screw-like motion, while the lower plate rotates in the opposite direction. The object of the spiral is to hold the scraper which is placed where the edges of the two plates, which have not a vertical axis, meet. To clean the machine we remove the spindle, funnel and plates, and the spiral from the inside of the spindle.

Roller Machines.

The best makes of paint-mill are those which act by means of rollers made of various hard substances. They are

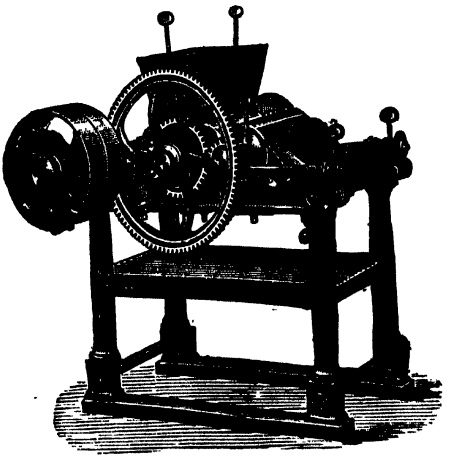


Fig. 54.

certainly rather expensive, but they make up so fully for that by the fineness of the colour they produce and by the magnitude of their output that no colour factory is complete without them. For artistic painting they give colours rubbed finer than is possible with any other system.

Fig. 54 shows the roller machine of J. M. Lehmann for printing and lithographic inks, and oil paint. The various sizes of this machine include three very finely polished rollers of green porphyry, which are harder than steel, and have

the property of clinging to the colour, whereby great fineness of colour and large yield are ensured. If the machine is rightly handled the colour cannot escape at the ends of the rollers. Unequal speeds are imparted to the rollers, and the front one has also a lateral motion. One very valuable character of the machine is that at the end of the work the porphyry rollers run off quite clean, so that they waste no appreciable amount even of quite small charges, which can therefore be taken by the larger sizes of mill.

The paint, etc., is poured between the first and the second roller, and is rubbed fine by the stones, passing to the scraper, which delivers it into a receptacle placed below the mill.

The enormous output of these machines may be illustrated by the following figures:—

No. 1	delivers	about	3,000	kilos.	white lead	or	200	kilos.	printing ink
„ 2	„	„	2,500	„	„		150	„	„ „
„ 3	„	„	1,500	„	„		100	„	„ „
„ 4	„	„	1,000	„	„		70	„	„ „

per day, and other pigments in proportion. This is with the finest grinding. The four sizes require 2½, 1½, 1, and ½ h.p. respectively. Other sizes are made for hand-power, *e.g.*, No. 5, which will deal with 300 kilos. of white lead daily.

Similar machines are built by H. F. Stolberg of Offenbach a. M., Beyer Frères of Paris, and others, but Lehmann has the best reputation in Germany and Austria, and his machines are practical and well made.

The fineness demanded of the colour naturally affects the output and it is unreasonable to expect a machine to deliver as much fine colour for art work as it will coarser colour for house-painting, independently of the great toughness, and many things, such as printers' ink. This too has an effect upon the output of any mill. The striking difference made in the output of Lehmann's machine by using it for printing ink instead of white lead, as given above, shows this very clearly.

CHAPTER XVIII.

MANUFACTURE OF HOUSE OIL PAINTS.

ORDINARY house paint consists of pigment and vehicle. The latter may be according to circumstances linseed oil, bleached linseed oil, boiled oil, or bleached boiled oil. Both the essential parts of the paint must have certain qualities to produce a good, usable, and durable paint, which may be stated as follows:—

We require of the pigment:—

1. That it should be perfectly dry.

2. That it should be in the finest possible powder, without admixture of sand, and that it should feel soft to the fingers.

3. That it should be as free from adulteration as is consistent with the price paid for it.

4. That it should have the necessary fastness to light and air.

5. That it should have sufficient body.

We require from the vehicle:—

1. That it should have the proper consistency, neither too thin nor too thick. If it errs in the second particular, the paint will not go on easily with the brush; if in the first, the colour will not stick on, and is apt on inclined or vertical surfaces to run down before it dries.

2. That it should not perceptibly affect the colour of the paint, especially when that is to be white.

3. That it should dry properly.

4. That it gets hard, and has a sufficient resistance to weather and atmospheric influences.

Raw and boiled linseed oil, exposed to the action of the air,

alter by oxidation and the heat of the sun. Free linoleic acid becomes linoxic acid, the undecomposed linoleine becomes linoxin. The coat thus formed is durable and resistant to outward influences, but after a long time the linoxin itself decomposes, becomes brittle, and flakes off.

Linseed oil itself is the best vehicle for pigments, but it dries too slowly, and must therefore be replaced by boiled linseed oil. The driers added to the oil during the boil make it dry not only quicker but harder, while at the same time, especially with lead driers, they make the coat less durable than if the raw oil had been used alone.

The qualities to be demanded of a house paint may be divided into those which can be recognised by inspecting the paint, and those which can only be known by its behaviour after use. In the first class we have four properties:—

1. That the paint has the proper consistency, *i.e.*, is ready for the immediate use of the brush, and can be applied to the surface to be coated in a satisfactory manner.

2. That the paint has been properly rubbed up. Every particle of the pigment must be wrapped up in the vehicle and be penetrated by it, so that the whole is like an ointment, perfectly uniform and free from perceptible grains.

3. That the paint dries quickly and hard enough.

4. That the paint covers well enough. It must be of sufficient body to conceal entirely the surface to which it is applied.

In the second class we have three properties:—

1. The paint must not injure the surface to which it is applied, either by its own chemical properties, or by its own in conjunction with those of the vehicle, whether by galvanic action or otherwise. Neither on the other hand must there be any appreciable effect exerted on the paint by the surface to which it is applied.

2. The paint must adhere well to the surface painted, and must at the same time be elastic enough to prevent changes

of temperature from producing cracks by alternate contraction and expansion.

3. The paint must be durable, *i.e.*, must resist the destructive influences of the environment, whether they are mechanical or chemical, and must form a coat hard enough to permit of being cleaned and polished.

To make the paint answer all these conditions, however, something more is necessary than depends upon the paint, *viz.*:—

1. The vehicle must be chosen with care and with reference to the use the paint is to subserve. This choice is dependent partly on the nature of the surface to be painted and partly on the influences to which it is subsequently to be subjected.

2. The materials used must be pure and suitable for the object of the painting.

3. The application of the paint must be done in a careful and workmanlike manner.

We can now see that before a paint can be pronounced good a whole list of requirements must be satisfied, and also that it may not be the fault of a paint that it does not answer, if it has been improperly used.

Assuming that the pigment has been properly chosen, I proceed to the manufacture of oil-paints, *i.e.*, to the mixing of the pigment with the vehicle. All pigments must be in a proper condition before they go to the paint-mills, because the machine is not intended to mix and grind at the same time. On a small scale we stir the pigment a little at a time into raw or boiled linseed oil until we have a perfect mixture in which no solid matter is distinguishable. On a large scale we use one of the machines already described.

As regards the proportion between vehicle and pigment, it must be remarked that the paints of commerce are usually mixed very thick, partly because it is to the interest of the manufacturer to use as little vehicle as possible, because the vehicle is usually dearer than the pigment, and partly because

consumers think that a thick paint is better than a thin one, and also because thick paints are better for sending to a distance. These circumstances have to be carefully borne in mind. If we want thin paints, the process of mixing is very easy. We simply take the pigment and stir it up in as much vehicle as is necessary till we get a uniform product. It is, however, quite another matter to make a thick paint, *i.e.*, pigments containing no more liquid than is necessary to make them into a paste, so that they can be diluted just before use. In making such paints we soon find that there is an excess of pigment over vehicle which cannot be exceeded, and which in any case makes the mixing more and more difficult, and makes it require more time and more power. Certain pigments, such as the ochres, require far more vehicle than others, but the manufacturer, on account of the greater price of the vehicle, uses only from two-thirds to three-quarters of the weight of the pigment. This being the case with the lighter pigments, the heavier ones, such as lead and chrome colours, want even less vehicle. With these a weight of vehicle amounting to one-quarter to one-third of the weight of the pigment will give thick paints.

It is often impossible for the paint manufacturer to deliver pure paints for the price, and he has therefore to thin with heavyspar. If in his dealings with the pigment manufacturer he buys only cheap kinds he gets the heavyspar in without having the trouble of getting it and mixing it in himself, although he had better do so. In these cases it is very hard to draw a line between adulterated and unadulterated goods, and a pigment can then only be regarded as the latter when it contains foreign ingredients out of all proportion with its price.

When the mixing has been perfectly done, the mixture is put through the paint mill, where it is brought to the desired degree of fineness. In special cases, where extra fineness is needed, the paint must be put twice or even three times through the paint mill.

I now give various recipes for particular mixed paints, which would require too much space to specify more particularly.

White Lead Pigments.

	Kilos.
Pure white lead in powder	28
Bleached or ordinary linseed oil	6
Pure white lead in powder	18
Pure white heavyspar	5
Linseed oil	5
Pure white lead in powder	18
Pure white heavyspar	5
Linseed oil	7
Pure white lead in powder	13
Pure white heavyspar	15
Linseed oil	13

Zinc White Pigments.

	Kilos.
Finest zinc white	11
Bleached or ordinary linseed oil	5
Finest zinc white	11
Pure white heavyspar	6
Linseed oil	7

Grey Colours

are made by mixing any of the above whites with a black such as graphite or lampblack, or with a blue such as ultramarine or Prussian blue, or an ochre.

Yellow Pigments.

	Kilos.
Ochre	33
Heavyspar	15
Boiled oil	18
Ochre	25
Pure white lead	6
Boiled oil	10

	Kilos.
Pure white lead	6
Ochre	25
Heavyspar	26
Boiled oil	13
Chrome yellow	10
Boiled oil	7
Chrome yellow	30
White lead	5
Heavyspar	15
Boiled oil	21

Red Pigments.

	Kilos.
Red lead	30
Heavyspar	22
Boiled oil	12
Venetian red	10
Heavyspar	5
Boiled oil	5
Venetian red	20
Heavyspar	10
Ochre	10
Boiled oil	18
Cinnabar	10
Chrome orange	10
Linseed oil	6

Green Pigments.

	Kilo
Chrome green	11
Boiled oil	4
Chrome green	11
Boiled oil	6
Heavyspar	5
Schweinfurt green	18
Zinc white	12
Boiled oil	8
Zinc green	20
Boiled oil	7

Blue Pigments.

	Kilos.
Ultramarine blue	7
Zinc white	10
Boiled oil	6
Ultramarine blue	7
Zinc white	10
Heavyspar	5
Boiled oil	8
Prussian blue	10
Zinc white	5
Boiled oil	8

Brown Pigments.

	Kilos.
Umber	21
Boiled oil	8
Umber	21
Heavyspar	10
Boiled oil	10
Velvet brown	15
Boiled oil	8
Filling up[1]	20
Boiled oil	8

Black Pigments.

	Kilos.
Vegetable black	22
Boiled oil	10
Vegetable black	11
Heavyspar	5
Boiled oil	6
Lampblack	10
Boiled oil	11

[1] *Sic* in the original.—Tr.

Hugoulin's Process.

We prepare in a glass or earthenware vessel a thin homogeneous paste with water and one of the following substances in fine powder in the proportions given.

To 1,000 kilos.	white zinc oxide	300-400	kilos.	water	
,, ,, ,,	grey ,, ,,	150-180	,,	,,	
,, ,, ,,	white lead	150-180	,,	,,	
,, ,, ,,	red lead	80-160	,,	,,	
,, ,, ,,	lampblack	about 1,000	,,	,,	

To this paste we add enough linseed oil to make a consistent colour by thorough stirring until the oil has taken the pigment from the water. The water is then decanted from above the mass, which is then kneaded up exactly like butter to get all the water out of it. Finally a greasy mass remains, which, when it has to be used, is diluted to painting consistency with oil. This colour is shown by the throwing out of the water to be a true compound (this it is not, but the pigment has more tendency to mix with oil than with water)[1] and has all the appearance of one. If other minerals than those given are used, *e.g.*, ochre, earth-colours, copper compounds, etc., no throwing out of water takes place and however long we stir, the mass remains a mixture of oil, water and pigment. Combination only takes place beween linseed oil and white or red lead, white or grey zinc oxide, or chrome yellow, or lampblack, whereby the preference that these pigments enjoy as a consequence of practical experience of their power of protecting wood and metal is explained.

The process for making these house paints on any scale, small or large, is as follows: One of the above-mentioned pigments is worked to a paste with water and a wooden spatula. This paste is then thinned with more water, and run through a silk sieve. It is best to have the paste very thin so that it will flow freely through the sieve. The sieve usually

[1] This is evidently an interjection of Andes in a quotation from a specification.

keeps back about ½ per cent. of the pigment, which is kept for further grinding, and also any impurities which may have been present, and which neither the paint-mill nor the muller is competent to get rid of.

The filtered paste is allowed to stand in a vessel to settle, which may take any time from a few hours to a few days. The water is then run off, and the pigment is stirred up with oil for a few minutes. The paste balls together at the bottom of the vessel. The kneading is then done, and all the remaining water squeezed out of the mass and poured away. Just before use the colour is properly thinned with oil and siccative. By the above-described process a single workman can turn out over 100 kilos. of faultless oil paint within two hours.

The new process is already used to a fairly large extent in cases where it is a question of making several hundred kilos. of oil paint at a time, and has always given excellent results. When it becomes further extended it will perhaps be found convenient to bring pigments on the market in the form of the pastes that it requires instead of in the usual dry form.

Zinc grey must be put through the sieve dry, because it oxidises by long contact with water and forms a solid mass which will not easily combine with oil. Lampblack is not wetted by water, so that in its case 10 per cent. of alcohol must be added to the water. The lampblack is mixed with this dilute spirit till it has the dampness of fresh snuff. In this form it mingles readily with water. It is then treated as above by decanting the water, stirring up with oil, and kneading out the remaining water.

Process for Making Weather-Proof Paint for Walls.

The process of E. G. Thenn (D.R.P. 25,137) is as follows: Mix and grind thoroughly in a mill a mass consisting of 20 per cent. dry silicate of potash, 10 per cent. felspar, 27 per

cent. artificially precipitated silicic hydrate, 90 per cent. cryolite, 14 per cent. of any natural silicate readily attackable by caustic potash lye, *e.g.*, pumice, and 19 per cent. of crystallised carbonate of potash. This mixture is then mixed with about half its weight of pure well-levigated earth-colour, or other pigment not affected by caustic lime or potash. The whole mass is thoroughly mixed and sieved through a sieve with 600 meshes to one square centimetre.

The vehicle consists of thick milk of lime which has been passed through a sieve of the same fineness as the dry mass, and is added to the dry mass in the proportions of about 2 vols. of milk of lime to 1 of pigment. The whole mass is then put again through the sieve.

The colour is applied like an ordinary lime-wash. When dry, which takes about twenty-four hours, the surface is gone over with clean water several times to accelerate its hardening. This object is attained still sooner if the water is used hot. Rain and natural dampness of the air have, of course, the same effect. If the paint has to resist unusual severe mechanical influences, it is a good plan to harden with a 15 per cent. solution of potash waterglass instead of with plain water.

The hardening action consists essentially in the formation of silicate of lime, formed by the interaction of the silicate of potash and carbonate of lime. The advantages of the application are its resistance to weather, cheapness, handsome appearance and washability.

Universal Pigment for Use as Water, Oil or Lake Colour.

By the process of J. Strenli & Co., of Horgen, a colour is obtained which can be used with oil or water, or as a lake colour, and may therefore be called universal. Dissolve 1 kilo. of raw caoutchouc in small pieces, by heating it with about 20 kilos. of linseed oil. At the same time boil 2½ kilos.

of Panama wood[1] or flax-seeds in 100 kilos. of water for about half an hour. We thus get a decoction having an oily character in virtue of the flax seeds used, which is intended to facilitate saponification of the materials. Panama wood has the advantage that a colour rubbed up with a mixture containing it adheres very strongly to the painted objects, whether they are of wood, stone or iron. Besides its extract is very much like the purest soapy water whereby intimate union with the indiarubber solution is much facilitated.

While this decoction is boiling, the indiarubber solution is diluted at a temperature of about 100° C. with more linseed oil, in the proportion of about five times its volume. This dilute indiarubber solution is then mixed with four-thirds of its own volume of the decoction, and well stirred up with it to a thin soapy liquid. The dry pigment is then diligently stirred up in it till a paste is produced which can be rubbed up in the paint mill, through which it is at once put. Only chemically pure pigments can be used for making this universal colour, for if, for example, heavyspar is added, it is impossible to get a uniform mixture. The oil would unite with the pigment and the heavyspar and the water would be thrown out, and the result would not be a universal colour but an ordinary oil-colour.

On leaving the paint-mill, the universal colour is ready, and can be delivered up to the painter for further manipulation.

The materials contained in the universal colour permit of its uniting easily with water, oil, or varnish, so that the painter can mix it with water and so get water colour or distemper, or with oil and so get an oil colour, or with varnish and so get a coloured varnish. As distemper, the colours are durable and not liable to mouldiness; as oil colours, they form no surface-skin, and without the use of wax give a very

[1] Quillaia bark.

fine and durable coat which can be washed with soap or soda. It is cheap as it does not contain wax.

The colours got in the manner just described set harder than ordinary ones, resist weather, and can be used in or out of doors either in winter or summer.

Grunzweig's Oil Paint.

Grunzweig mixes a paint consisting of 10 per cent. umber, 5 per cent. yellow ochre, 10 per cent. red lead, 5 per cent. ultramarine, 5 per cent. zinc white, 25 per cent. white lead, 10 per cent. of graphite, and 25 per cent. of boiled oil.

The surface to be painted with this must have been carefully cleaned and dried, and if of iron must have been freed from rust. The mass can be diluted with boiled oil only. This heterogeneous colour has probably been patented in England, so that it may be called "patent".

To Make Oil Colours Resist High Temperatures.

This object is realised, according to D.R.P. 17,459, by using a solution of shellac, camphor and boiled oil in spirit. The tincture is made paler by treatment with chalk. The surface to be painted is grounded with a mixture of this tincture with plaster of Paris, and then painted with pigment rubbed up with the tincture.

Glasenapp's Black Paint.

This is not exactly a black but rather a dark grey, but has very great body. It was invented by Glasenapp.

100 lb. of boiled oil made with lead are heated till they begin to fume, and then 15 lb. of litharge or red lead are gradually added and digested to complete solution. We then add gradually 1½ lb. of flowers of sulphur and stir diligently. Finally we add 2 lb. more of the lead oxide and continue the heat for thirty to sixty minutes longer, to get all the sulphur (which dissolves readily in the oil) into combination.

The final rather thick liquid is thinned with oil of turpentine. This application rightly made will dry in ten hours, but if there is any uncombined sulphur it will take longer. The presence of free sulphur in the unfinished paint may be known by the gases given off having a characteristic and disagreeable smell. The sulphide of lead gradually settles, but the paint is easily made fit for use by stirring it up.

Vehicle and Fixer for House Paints.

The invention (D.R.P. 3,420) consists in mixing organic or inorganic colouring matters with the following paste:—

Glue, 25 grammes; glycerine, 534 grammes; water, 208 grammes; ammonia, 12½ grammes; wax, 208 grammes; and resin, 12½ grammes. Paints made with this vehicle are suitable for a variety of industrial purposes. They form an advantageous substitute for pastels, and are usable for both oil and water colour painting. They are easily applied to fabrics, and also to porcelain, earthenware, etc. By dint of these properties, and their rapid drying, they are of great value to landscape painters. The paste is made as follows:—

Mix by heating together 208 grammes of pure white wax and about 260 of glycerine. When the wax is quite fused, a solution of 12½ grammes of resin in ether is added. Finally we add a solution of 25 grammes of fish or other glue in about 260 grammes of glycerine. Then dilute with water and stir till cold. The paste is then rubbed up with the pigments and the paint is ready. The amount of glycerine used has to be regulated according to the drying power the paint is to have.

Preparation of a Substitute for Linseed or Turpentine Oil.

This oil extract (D.R.P. 3,420) is made from colophony free from turpentine, crystal soda, liquid ammonia and water, and is a syrupy mass which can be used with great advantage in house painting. The product is made as follows:—

100 lb. of the colophony, 20 of crystal soda and 50 of water are boiled together, and then mixed intimately with 250 of water and 24 of ammonia.

The resulting product can be used with great success in the manufacture of all paints as a substitute for oil of turpentine or linseed, and the pigments simply need to be rubbed up with it.

The paint so got has the property of drying quickly and easily without any siccative, and can readily be varnished over. The coats withstand changes of temperature perfectly, keep under water as well as dry and get very hard. Paints made with this substitute can be diluted at will simply with water, even to be very thinly flowing indeed. In comparison with the methods hitherto known of making house paints with linseed or turpentine oil, this substitute has the important advantage that it can be made at one-third of the cost of the original vehicle, and gives a still more durable coat.

Bruchhold's Weatherproof Paint.

Bruchhold's new paint consists of boiled oil which must be free from every artificial siccative, with a little oil of creosote and powdered silver slag from a silver refinery. The exact proportions are:—

	Per cent.
Slag	75
Boiled oil	24
Creosote	1

The essential ingredient is the slag, the great hardness of which gives the paint much resistance to water or acid, and contains no metals liable to oxidation.

Kallkolith.

Under this name a product has been for some years on the market as a paint, having been ostensibly discovered by Otto Kall of Heidelberg.

Kallkolith is used with great advantage as a substitute

for the usual priming colours on wood and iron, and instead of boiled oil on stone, cement and all kinds of plaster. It prevents all blistering and gives an exceedingly hard, smooth and durable surface, as it combines firmly not only with the surface but with the paint subsequently laid over it. It has the following advantages:—

1. *Cheapness.*—It is half the price of ordinary priming and linseed oil.

2. *Yield.*—It goes three times as far as ordinary priming.

3. *Convenience.*—It is very easily applied and with great economy of pigment, which is made to cover well in the thinnest coats, and will have more durability than on an ordinary oil priming.

4. *Drying powers.*—The drying only takes two to three hours. Hence we have

5. *Continuance* of the work ensured.

6. *Oil colours* on kallkolith on wood and plaster have greater beauty and

7. *Greater durability* and specially very great

8. *Hardness*, so that, as the experience of several years has shown, the lasting of the substance on outside fronts exposed to the weather is most satisfactory. Hence any work done with kallkolith may be fully guaranteed.

On wood, kallkolith is applied thinly and with care. It dries in from one to two hours and the smoothing with pumice may be omitted, only brushing when dry with a brush before stopping. We thus get a solid, smooth surface with great saving of time, and one coat of good oil paint will be found to have all the body required. This single coat is sandpapered and dusted, and the finishing colour can now be laid on, and will remain perfectly bright. A dull wax paint can also be used, and one coat of it will be enough on a priming of kallkolith.

Woodwork, preserved in its natural colour by kallkolith, acquires, when the application has been carefully made,

a fine, antique shade, and can be waxed, varnished or polished over the kallkolith.

If the objects are to be decorated, they can be painted on with kallkolith and beautiful work can be done in this way. In polishing the wood we proceed as follows: If the wood is to retain its natural colour, from one to three coats of kallkolith are applied, according as the wood has fine or coarse pores, and when dry sandpapered is polished in the usual way. If a deeper colour of the wood is wanted, a larger number of kallkolith coats is applied, and the surface is well rubbed with soft paper before polishing.

Poker-work and intarsia can be imitated with great fidelity on soft as well as on hard wood. To do this, kallkolith is painted on the wood, diluting it for light tints and putting in the shadows afterwards with undiluted kallkolith.

In imitating other woods, it is advisable to mix the graining colours with kallkolith and water instead of vinegar. The kallkolith completely prevents any creeping on to the oil ground, thereby saving a good deal of time, and has the additional advantage that when the work is varnished less varnish is required to give the proper lustre.

As a priming for oil colours on iron, kallkolith is applied thinly and carefully.

As a priming for oil colours on stone, cement and plaster, instead of boiled oil, kallkolith is used diluted with twice its volume of water. The surface is carefully dried, and freed from dust, and then the diluted kallkolith is applied fully, and with as little frothing as possible, with large brushes. In favourable weather, the application dries in from one to two hours, and then can be at once thinly covered with any paint. If the work is carefully done, as good and durable an effect can be produced as in any other way, and with much less time and labour.

Old weather-worn oil-painted fronts can be saved from the

need of having the paint fully renewed if they are well cleaned and then painted with dilute kallkolith. Kallkolith is applied to cement exactly as to plaster, but the plaster should be dry, and the kallkolith should be applied during fine weather. All lime-washed fronts must be well scraped and washed, and should then be painted over with kallkolith diluted with seven times its volume of water, and then, when that is dry, treated as if they were fresh plaster.

As a priming for distemper instead of soap kallkolith is used diluted with seven times its volume of water, and the distempering is done as usual when the kallkolith is dry, although the distemper colour should be a little thinner than usual. It does no harm if the priming has for any reason to stand uncovered for a time, which cannot be allowed with a priming that wants sand-papering.

For preparing walls for decoration kallkolith is used diluted with seven times its volume of cold water. For this purpose it has the advantage that the decorative painting is more durable on it than on size. Kallkolith comes on the market as a thickish dark brownish-red liquid, which on shaking becomes covered with a soapy lather and has a very disagreeable ammoniacal smell. The colour alone seems to be rather a drawback to its use, and its nauseous smell, which of course becomes very obvious when painting is done with it, must in my opinion entirely prevent its use in some cases.

I have mentioned in a former work that Dr. von Scherzer brought about thirty years ago from China a cement or paint called schio-laio, consisting of pig's blood, quicklime and alum, and specially used for painting boxes and other articles of wood to make them waterproof both within and without. It has long been known that all albuminous bodies make compounds with lime which are excellent for paint, and blood is no exception to the rule. The German Government had analyses made of schio-laio, to determine the recipe if possible, and then to make some and experiment with it.

According to the determinations of nitrogen and lime, the proportion between fresh blood and slaked lime was put at three to four, and in fact if we mix 3 lb. of whipped or defibrinated blood with 4 lb. of lime, slaked to a powder, we get a thin tenacious mass. With more lime the mass is thicker, and quite as tenacious as before.

In accordance with these researches, I have drawn up the following formula for a vehicle:—

Whipped fresh blood	5 lb.
Slaked lime	1½ lb.
Water	1 gal.

This composition can be mixed with all manner of paints, except white, and acts as a vehicle for them.

Kall's patent (D.R.P. 18,307) says: To 10 lb. of whipped blood from the slaughter-house add through a sieve 1 lb. of old quicklime which has fallen to dust, stir, and let the mixture stand for twenty-four hours. Then skim the impurities off from the surface, remove the rest from the sediment and put it aside, and stir up the latter with water and allow it to settle. Then pour the water off into what has been put on one side, so as to dilute it. Let the mass then stand quiet for from ten to twelve days after mixing it with a solution of permanganate of potash, which partly bleaches it and prevents it from turning mouldy.

At the end of this time the mass is stirred up and more water is added till it is of the consistency of quite thin glue. It is best, to secure uniformity of mixture, always to get a predetermined gravity by means of a hydrometer.

This liquid is filtered, mixed with a little oil of lavender, and kept in well-closed casks, when it will keep for a very long time.

CHAPTER XIX.

SHIP PAINTS.

A good paint for hulls of ships, in iron or steel, to resist water, has not only to preserve the material in the ordinary way, but to prevent the growth of sea-weeds and animals upon it.

This object is attained by smooth hard-clinging coats which contain substances poisonous to sea-growths, both vegetable and animal, and have also the property after they have killed the organisms of flaking off and leaving the hull bare.

There are already poisonous paints known, but they will not flake off, and the shell fish, etc., make as much friction as the ship moves when dead as they did when living. On the other hand paints are known which slowly flake off, but they are not poisonous, and allow the organisms to attain considerable development before flaking off.

Schnittger's Paint.

Schnittger's process seeks to combine both properties in one paint, and is in this respect chiefly to be regarded as a novelty. The manufacture of it proceeds as follows:—

Take 100 lb. of copal, and heat it till it has lessened to about 80 lb., and condense and retain the fumes, stirring during the heating with a suitable stirrer. When the distillation is over the copal is removed from the still so as to cool as quickly as possible. It is a good plan to run it into cold water. When cold the copal is broken up and dissolved by heating it on a sandbath in 96 per cent. spirit, at as low a temperature as possible. The oil which came over during

the distillation is added to the solution, but not the water which would cause precipitation, whereupon the whole is then filtered. In the meantime the following solutions in spirit are prepared:—

Of 20 lb. powdered aloes in 40 lb. of 96 per cent. spirit; of 20 lb. Japan camphor in 40 lb. of 96 per cent. spirit; of 20 lb. pitch in 40 lb. of 96 per cent. spirit; and of 50 lb. colophony in 30 lb. of 96 per cent. spirit. These four tinctures are then mixed into the copal solution, cleared by allowing time to settle, and then the whole is decanted from the sediment.

To this carefully prepared solution we add, with continual stirring, for every 33 lb. of it 28 lb. of caput mortuum, 3 lb. linseed oil, 3 lb. castor oil, and finally, after long stirring, 10 lb. of red oxide of mercury; stir for two hours more, and then add 5 lb. of crystallised carbolic acid. After mixing this in, leave to stand for twenty-four hours and pack into casks.

Paint for Ships, and Submarine Constructions.

In the process of Bessy G. Benedict and Frank Lee Benedict of Viareggio, copper sulphate is reduced with grape sugar and caustic potash. The precipitate of cuprous oxide is mixed with carbolic acid, gently heated, and mixed with linseed oil and mineral pigments. A cuprous phenylate is said to be formed and to be very poisonous to animal and vegetable life.

Paint for Iron Ships.

600 kilos. of asphalt or black pitch are mixed warm with 480 lb. of boiled linseed oil. The mixture is cooled to 24° F., and to it is added a mixture of 600 kilos. graphite, 120 kilos. arsenite of copper and 640 kilos. of purified coal-tar oil. The whole is thoroughly mixed and applied to the hull in several coats. The arsenic in it is said to prevent the growth of barnacles, etc., on the ship.

CHAPTER XX.

LUMINOUS PAINT.

LUMINOUS paint is a product which excites much interest, and meeting with much false judgment is distrusted by many people. It is therefore a matter of common interest to give below the results of accurate investigations, which lead us to form a correct opinion on the question.

The attempts to make a luminous paint date very far back, and the Chinese are said to have been able to make from the most remote antiquity a paint out of oyster-shells and sulphur which shone in the dark. At the same time such things used to be looked upon as playthings, as they were too inefficient and too expensive for practical use on a large scale.

The first to succeed in making luminous paint which would glow even under oil or water on a large scale was Balmain, a native of Heligoland. Then and not before did such paints become of practical value. The price of such colours, which was M. 110 per lb. seven years ago, has now been brought down to one-twenty-fifth of that by improved machinery and methods of manufacture.

In chemical composition the paint is a compound of alkaline earth, sulphur, oxygen and a little water. It contains no phosphorus. Chemical analysis alone, however, is no criterion of its quality, as the light-giving power depends not only on proper composition but on a particular kind of molecular aggregation. It has consequently been found impossible to imitate Balmain's paint, now made by an English company which has acquired the patent.

Balmain's luminous paint, which can be had either as an oil or a water colour, has the remarkable property of, as it were, storing daylight or other strong light, and giving it out again in the dark, and is so excessively sensitive to light that a single spark from an induction coil will at once make it luminous. The power of the paint to give out light depends upon the power and duration of the light to which it has been previously exposed, as well as upon the mass of the paint itself, for the light penetrates through the whole mass of paint, and neither acts on nor proceeds from the surface only.

Hence the thicker the colour is laid on, and the longer lasting and more powerful the light which has acted upon it has been, the longer and stronger it will shine in the dark. If suddenly brought from light to darkness the paint first glows with a violet light, which finally becomes white, and then gradually gets weaker and weaker until the stock of stored-up energy is entirely expended.

If the paint is then brought from darkness to light it begins to store up again, and if exposed during the daytime it will absorb enough to shine throughout the longest winter night. Accumulation of dirt on the surface naturally hinders both absorption and radiation. Heat has a special effect upon luminous paint, and by making the light it gives out stronger only allows it to last for a correspondingly shorter time.

Hydrochloric and nitric acids destroy the luminosity as to varnishes, vehicles and pigments containing lead, so that as a vehicle and as a protection for luminous paint special preparations are needed, and if anything has to be written on the surface a special pigment must be used.

Objects which are already painted with an ordinary oil colour must be primed with a neutral ground colour before having luminous paint applied to them. Such a priming is cheap, and it is to be recommended even on unpainted surfaces if they are rough or porous, as they enable the luminous

paint to appear to much greater advantage by giving it a smooth surface. Three coats of luminous paint are enough in all cases, and it is at least as durable as the best oil paint, especially when varnished over by a suitable varnish. One pound of luminous paint will cover with three coats an area of twelve square feet.

Luminous water colour has the same general properties as the oil paint. But like all water colours it should only be used indoors, and not in the open air or on objects exposed to the weather. It is sold as a dry powder which is stirred up with a litre and a half of lukewarm water to every 10 lb. of pigment. The resulting mixture is enough to give three coats to 70 square feet of surface. Objects of unpainted wood, plaster, papier-mâché, etc., are grounded before the application of luminous paint with a solution of pure gelatine in 12 parts of hot water, to fill the pores and prevent waste of the luminous paint. Luminous paint must be applied with perfectly clean brushes and must be kept stirred up during use. Every coat must be dry before another is laid on.

Although success is certain when a luminous paint has been used with rigid attentions to the directions, it is important to note that it is only properly effective in real darkness. Where there is partial light or in artificial light the effect is spoiled and the use of the paint only leads to mistaken judgment. It would, for example, be folly in towns which are lighted at night, while a finger-post by a country roadside needs merely the application of luminous paint to make it as useful by night as by day.

Many trials made with luminous paint in unsuitable places have caused it to be depreciated. It must be remembered, too, that a luminous paint only shines by emitting stored energy, and must consequently be afforded the necessary intervals for renewing its stock, if it is to continue to be of service. At the entrances of and inside dark rooms in which

highly inflammable goods are stored it is an excellent plan to use placards painted in luminous paint, only remembering that they must be exposed to daylight at intervals. They should therefore be placed where they are exposed to light in the daytime, or they may be made movable so that they can be taken out of the room occasionally. They will then allow people to go about freely in the darkened room and save much time and trouble.

As luminous paint shines equally well under water, divers can work in deep water, if their apparatus is painted with luminous paint. Mr. Hedger, of the Southampton Dock Company, in a report on the raising of a ship sunk off that port, states that by means of luminous paint the divers were able to see the seams and bolts in the hull at a depth of eight metres well enough to be able to work with ease. It is possible for an object which has been exposed to a corresponding day's light to be recognised at the end of a following fifteen hours' night so much that large and clear writing can be distinctly read.

Most people know from experience how convenient the use of luminous paint is on many small objects, such as match-boxes, lamp-shades, door-signs, etc., as it enables them to be found in the dark, and besides these uses of luminous paints there are others which show the great advantages of them, and which will now be briefly mentioned.

For navigation purposes: buoys painted with luminous paint can be clearly seen 200 metres off in the darkest night and so show the way. Many lives would be saved if life belts were painted with luminous paint so that a drowning person could see by night the belt thrown over to him. What other chance has he of finding it? The paint is also good for the piers of bridges, piles, lightships, railings, etc., etc.

On railways: for painting the insides of goods trucks, indicating level boards, numbers, level crossings which are

not lighted, all of which can then be seen at a distance, and people can see whether gates are shut or not.

In the country: for painting finger-posts, milestones, notice boards, etc., in places destitute of artificial light and in country towns for the names of streets, the numbers of houses, hydrants, etc.

In military works: for painting objects destined for use in engineering works, such as piles, etc., and for making out the profiles and outlines of such works.

In stores of gunpowder, spirit, petroleum, and the painting inside mines, ships' holds and other dark localities where there is fire-risk, we use tablets painted with luminous paint that can be removed on occasion so as to get the necessary exposure to daylight. These tablets may be of wood, glass, or zinc, and enable short jobs to be done in such places without the risk attending the use of lamps.

Luminous paints cannot be too much recommended for theatres, factories and other places where large crowds assemble, to indicate exits and give other directions. If by any chance the ordinary illumination of the place should suddenly fail, every one can direct his steps with certainty.

Luminous water colours are specially good for room walls, ceilings, passages, staircases, which get daylight in the daytime and for painting the stairs themselves in barracks and hospitals. They can also be used in wall-paper-making and photography, and for painting all kinds of paper work, and generally all objects which are not usually in the open air.

Luminous paint is also made up with wax, and in this way is largely used by jewellers, makers of glass ornaments, and in making fish-bait.

The preparation of luminous paint is as follows:—

Oyster-shells are cleaned with warm water, and put in the fire for half an hour, then taken out, allowed to cool, ground, and freed from worthless grey particles. The powder is interstratified with layers of sulphur in a crucible, and the lid is

then luted on with a thick paste of sand and beer. When the crucible has been red-hot for an hour, it is allowed to cool. The white powder in it is then carefully sieved, and mixed with gum-water as a vehicle.

An invention patented by G. Schatte of Dresden some time ago has the object of preparing durable white or coloured paints which are luminous, but of which the colour remains the same in daylight. To effect this, Zanzibar or akuri copal is fused over a charcoal fire and 15 parts of the mass are dissolved in 60 parts of French oil of turpentine, filtered, and mixed with 25 parts of pure linseed oil which has been heated and partially cooled again. The varnish thus obtained is worked up into a luminous paint in a paint-mill by one of the following processes. Iron rollers must not be used, as any fragments of iron which got into the paint would impair its luminosity.

The varnish as sold almost always contains lead or manganese, which has a tendency to impair the luminosity of the calcium sulphide.

A pure white luminous paint is prepared by mixing 40 lb. of the above varnish with 6 lb. of prepared sulphate of barium, 6 lb. of prepared calcium carbonate, 12 lb. of prepared white zinc sulphite, and 36 lb. of good luminous calcium sulphide to an emulsion, and then making the whole very fine in the paint-mill.

A red luminous paint is prepared by mixing 50 lb. of the varnish with 8 lb. of prepared sulphate of barium, 2 lb. of prepared madder-lake, 6 lb. of prepared realgar (red sulphide of arsenic) and 34 lb. of good luminous calcium sulphide, worked up in the paint-mill.

For an orange paint, 46 lb. of the varnish are mixed with 17½ lb. of prepared barium sulphate, 1 lb. of prepared Indian yellow, 1½ lb. of prepared madder-lake and 34 lb. of good luminous calcium sulphide.

For a yellow paint, 48 lb. of the varnish are mixed with

10 lb. of prepared barium sulphate, 8 lb. of barium chromate, and 34 lb. of good luminous calcium sulphide.

For a green paint, 48 lb. of the varnish are mixed with 10 lb. of prepared barium sulphate, 8 lb. of chrome-green, 34 lb. of good luminous calcium sulphide.

For a blue paint, 42 lb. of the varnish are mixed with 10·2 of prepared barium sulphate, 6·4 of ultramarine, 5·4 of cobalt blue and 36 lb. of good luminous calcium sulphide.

For a violet paint, 42 lb. of the varnish are mixed with 10·2 lb. of prepared barium sulphite, 2·8 lb. of ultramarine violet, 9 lb. of arsenate of cobalt and 36 lb. of good luminous calcium sulphide.

For a grey paint, 45 lb. of the varnish are mixed with 6 lb. of prepared barium sulphate, 9 lb. of prepared carbonate of lime, ½ lb. of ultramarine blue, ½ lb. of zinc sulphite grey and 36 lb. of good luminous calcium sulphide.

For a yellowish-brown paint, 48 lb. of the varnish are mixed with 10 lb. of prepared barium sulphate, 8 lb. of orpiment and 34 lb. of good luminous calcium sulphide.

Luminous paints for artistic purposes are prepared by substituting for the varnish in the above recipes the same quantity of pure poppy oil and grinding especially fine.

For luminous oil paints, the varnish is replaced by an equal quantity of cold pressed linseed oil, thickened by boiling.

All the luminous paints above given can be used for coloured papers and other purposes by leaving out the varnish and grinding up the solids with water and a vehicle free from acid. Luminous wax paints can also be made for painting on glass vessels and the like, by substituting 10 per cent. of Japan wax, and 2½ per cent. of olive oil for the varnish. The so prepared wax-paints can be used on porcelain, which are then baked without access of air, or varnished over with waterglass.

CHAPTER XXI.

ARTISTS' COLOURS.

THESE include pigments rubbed up with poppy, linseed or nut oil, and used by artists for their special purposes, and the principles of their manufacture are the same as for ordinary oil paints. We only choose purer and more reliable pigments and are more particular in choosing the oil, and give the paints a much more thorough rubbing up in the paint-mill or with the muller.

With reference to pigments it must be remembered that we have now many more of them than formerly; it may be a question whether this is an advantage from an artistic point of view. Although in former times the choice of pigments was limited, they were at least reliable, and have lasted for centuries as fresh as at first. Now we have an untold number of pigments of every conceivable shade of which a large proportion change in a short time so much that the painter fails to recognise his own work.

With four pigments only, says John (*Die Malerei der Alten*, Berlin, 1846), *viz.*, white, Attic yellow ochre, Sinope red, and lampblack or ivory black, Apelles, Echion, Melanthus and Nicomachus, all very famous painters, executed those immortal works single specimens of which were the treasures of a city. Pliny, from whom this information is derived, continues as follows: "But now that purple glitters on the walls, and India sends us the mud of its rivers, and the blood of its dragons and elephants, noble painting has ceased to exist".

Among the Egyptians the number of paints which were allowed to be used for artistic purposes was limited, at first to five, but later to seven. The tools which served them for maulstick and palette at the same time show a row of seven hollows intended to receive the paints.

It would naturally take us too far to follow up the further increase in the number of pigments. The fact is that the masters of the old Italian and of the later Dutch schools knew and used a very considerable number of them. Even then artists used colours which have no pretension to permanency, and which the artists of to-day will not use. The oldest Florentine painters, for example, had not only real ultramarine, but biadetto or what we now call mountain blue, and indigo. For yellow they had massicot, for orange orpiment, besides gamboge and Naples yellow. Gamboge has now almost gone out of use in oil-painting. As a red they used pink from Brazil wood, as well as English red lead, dragon's blood, vermilion, and hematite or sinopia; for green they had verdigris and another copper-green. We also hear of a red called kermes,[1] as a rich English colour which was extracted out of dyed cloth imported from England. The Venetians seem to have used this as an oil paint at a very early period. Madder and cochineal were used in very early times, and also asphaltum, which first appears in the time of Titian; and we also have accounts of colours made from flowers, yellow from the crocus (saffron), red from violets, and pink from ivy-sap. Thus the number of colouring matters in use was continually increasing, and while the Egyptians, Assyrians, Pompeians and Herculaneans used as pigments first the natural earths and then those made from stones, and finally chemical compounds for the preparation of which no small skill is required, we find in the studios of the Middle Ages complete colour laboratories, because in those days the painters preferred to prepare their own colours.

[1] Closely allied to the cochineal insect.—Tr.

Now things have changed. The artist buys his colours from manufacturers, and it is no uncommon thing for price lists to contain the names of over 300 possible and impossible pigments, including shades which cannot be got except by the most desperate mixing. We also have whole series of lakes made with aniline dyes and alumina, which lose their colour very quickly when exposed to light, to say nothing of earth-pigments beautified with anilines, which have the same degree of durability. With regard to much of the material now offered by dealers to artists, the German Society for the Promotion of Rational Methods of Painting, which is located in Munich, has decided on fixing upon a scale of normal colours, in which only those colours which are known to be fast to light and air are included. Such alone should be used and the scale is here given:—

WHITES.

Kremser white, zinc white.

YELLOWS.

Pale Naples yellow, dark Naples yellow, reddish Naples yellow, pale and dark cadmium, orange cadmium, pale ochre, pale gold ochre, dark gold ochre, Sienna earth, Pozzuoli earth.

REDS.

Pale and dark English red, mountain cinnabar, Chinese cinnabar, patent cinnabar, dark and violet madder lake.

BROWNS.

Dark ochre, burnt dark ochre, burnt green ochre (Bohemian), burnt Sienna, Cyprian umber, burnt Cyprian umber, asphalt, mummein.

BLUES.

Cobalt blue, dark and light ultramarine, Prussian blue.

GREENS.

Warm chrome green, chrome green, pale and dark cobalt green, green Bohemian ochre, Veronese earth.

Blacks.

Ivory black, lampblack.

All these pigments, to be fit for artists' use, must be ground as fine as possible and be very carefully levigated so as to get a very soft and delicate powder. Thorough drying of this powder at from 80° to 100° C., until cessation of loss of weight shows that all water has been expelled, has been recommended of late, because the colour then requires much less oil, and this is, as we shall see presently, of great advantage to the purity of the tint.

As vehicles, the brothers Van Eyck in the fourteenth century used oil, so that they are the founders of painting in oils, as contrasted with the previous encaustic style, although it is now said that Heraclius, who lived in the tenth century, has left an account among many other secrets of the use of pigments with oil and even with boiled oil.

The oils chiefly used are linseed, poppy and nut oil, and there appears to be no doubt that many painters early employed in addition colophony and mastic, even amber and copal, and also wax, to make the pigments give a smooth mass. Baron von Tankenheim in 1770 proposed a pomatum-like composition of wax and oil (of which, however, no more detailed particulars are given) as a colour-vehicle; and Paillot de Montabert used a solution of wax in cold turpentine mixed with a little naphtha, and a little solution of copal and elemi in oil of turpentine.

The cause of these additions is to be found in the fact that many colours mixed with linseed, poppy, or nut oil, particularly the last, become tough on keeping, and thus very difficult to use. This occurs with lead-white and many of the earth-colours, and many heavy pigments, such as cinnabar, cannot be kept with oil alone, as their great specific gravity makes them settle out. In the making of oil paints, poppy and nut oil have shown themselves the best, because they contain

the least linoxyn ready made, and hence the destructive influences of air and light take longer to affect them than other drying oils. Nut oil cannot be used for all purposes, especially for whites or pale hues, on account of its dark colour, and bleached poppy and linseed oils have therefore to be used.

Pigments rubbed up thick with these oils, and having to be thinned for use, have other drawbacks besides the toughening. Among these are darkening of colour after use, whites turning yellow if deprived of light, slow drying and the unequal drying times of different colours, hardening from above downwards by the formation of a skin over the colour, and attempts to explain these matters seem to have shown that they are to a large extent due to the use of unnecessary quantities of oil.

"It seems paradoxical," says Professor Petruscheffsky of St. Petersburg, "but it is nevertheless true, that in oil painting as little oil should be used as possible." We should therefore use as far as we can such paints as contain the least oil, because it is only in that way we can avoid the above-mentioned troubles. As a proof that oil paints should be made up with as little oil as possible we may mention water colours, where very small quantities of gum or honey form a sufficient vehicle. As, however, the pigment cannot be used with only just sufficient oil to bind it, we must add something besides which is not oil, *e.g.*, an ethereal oil, such as oil of turpentine, of rosemary or lavender. When the colour is used, these evaporate, and the pigment is left with only the necessary amount of oil to bind it.

This explanation is most instructive, and shows that we must give up the old process of rubbing up pigments with a pure drying oil only, and introduce instead a method depending on the use of a mixed vehicle, consisting

1. Of drying oil with a varying amount of ethereal oil according to the nature of the pigment, or

2. Of drying oil, ethereal oil, and wax, or resin of a par-

ticular kind. This is the principle of the Mussini colours. As the various pigments have various drying powers with the same vehicle, care must be taken in the manufacture to mix such pigments as dry quickly (such as lead-pigments) with raw oil, and those which dry slowly with oil which has been boiled or otherwise made more drying. Great care is here necessary to use no lead compounds for making the oil drying, as the oil will then have a bad effect on the shade of certain pigments. Only pure manganese compounds should be used, and the oil should always be bleached afterwards in the sun to restore the original colour to the oil which has been darkened by the boiling.

Schnitger's Oil Paints.

According to the present practice, pigments for artists' use are rubbed up with oil, usually also with tallow or beeswax at the ordinary temperature, and in such proportions as to produce a mass of the consistency of butter.

As experience has shown, an oil paint has more durability and less tendency to darken the less oil has been used with the pigment.

(The first part of this assertion wants proof, as all our experience so far goes to show the contrary.)

The object of the process of P. C. Schnitger of Berlin is to lessen the amount of oil while still securing the necessary softness. The pigment is first mixed with the oil, but, in contrast with the practice hitherto prevailing, so as to make it thicker than it is to be when the paint is finished, and then has a preliminary passage through the paint-mill. The mass is then heated for some time, whereby it becomes first hard and brittle, and then again gradually softer and thinner, and finally tough. The heating is stopped at the soft stage and before toughness has set in, and the mass is quickly cooled.

It is not now, however, very suitable for further grinding, and has to be put through the mill several times at the

ordinary temperature. Finally, however, it acquires the necessary fineness, and can then be filled into tubes.

The duration of the heating and the temperature to be employed varies in different cases. Paints which will stand a high temperature without alteration of shade are heated, about a kilo. at a time, for two hours on the average, at a rather high temperature. The larger the mass heated at once the longer the heating must last.

To determine exactly whether the heating has lasted long enough, we take a small sample, cool it, and fill it into a tube, and see whether it can be pressed uniformly and easily out of the narrow orifice. If this is the case, the operation is finished. But if the paint only comes out by fits and starts, and requires great force, the heating must be continued. Paints which will not bear much heating, such as pale vegetable colours, are not to be heated above 100° C., and then take a day or two to finish. A few hours can be saved, however, by heating the mass under a high pressure of air.

To get this pressure, the vessel has to have only a little mass put into it and is closed with an air-tight cover. The expansion of the enclosed air on heating gives the pressure. Or a condensing pump may be used to force air into the vessel to any desired point. The test of the completion of the operation is the same as that given above.

The possible minimum of vehicle varies with the pigment and may be as high as 40 per cent. of the latter. The advantages of paints prepared by this method are:—

1. Less darkening on account of the small amount of oil used. 2. Greater body because there is a larger proportion of pigment in the paint. 3. The colours dry on the canvas, even where thick, much sooner and more evenly than ordinary paints, especially than those containing beeswax and tallow, when the interior remains soft long after the surface has dried. 4. Painting over is much sooner possible. 5. The colours in the tubes retain their consistency unchanged for long periods.

I do not think I can better characterise this process than by quoting the remarks of Dr. W. Reissig of Munich on the subject.

The expression "oil-vehicle" is here used in a sense which admits of many interpretations and is therefore unreliable. What is an oil-vehicle? If we rub up any pigment fine with linseed or other drying-oil, and paint with the mixture, it dries, even if slowly, to a solid mass—the paint. Here pure raw linseed oil is the vehicle. On the other hand we know that the drying is much quicker if the oil has been boiled, with or without driers, so as to get boiled oil. Is this —made from the oil—also an oil-vehicle; or only so when used without the addition of wax, etc.? It is therefore clear that it is not permissible to use the term in question, as we do not know what materials the inventor has taken to make his paints. A further important point is the manner, stated by the inventor, in which the pigments behave when heated with the oil-vehicle: "As the heating proceeds, the mixture becomes first hard and brittle, and then softer again". All this points to a decomposition occurring on account of the heat, and this is the more probable because "when the mass becomes soft again the heating must be stopped". A decomposition of the oil-vehicle with the pigment means either that the oil-vehicle is changed by the heat, or by chemical reaction with the hot pigment, or that the pigment itself is decomposed.

It is hence very probable that the oil has an altering action on the pigment. In this respect however various pigments must behave very differently, and nothing is said in the specification about anything of the kind. Science leads to the following conclusions. We know that certain mineral pigments, such as zinc oxide, ordinary lead-salts, etc., have the power of entering into combination with hot linseed oil and saponifying it. Others, however, and the greater number, have no action on heated linseed oil, the ochres for example.

But we must also here bear in mind that protracted heating alters the molecular constitution of bodies. This slightly affects the colour of pigments as a rule, and can only be excluded in the case of the process in question, when pigments are used for it which have been previously strongly heated, in their manufacture for example. Yellow iodide of mercury affords an example of this molecular change on heating. A temperature not far above 40° C. turns it red, and prolonged heating will convert soft transparent phosphorus into an opaque brown mass, the so-called amorphous phosphorus.

Such an action would certainly make the pigment more durable, because it would usually make it heavier and closer, just as great pressure would. These facts might give the process a very rational basis, but no allusion is made to them in the specification. Not a word is said about any change, however slight, in the colour of the heated paint, and as such changes would certainly occur with certain pigments, we can only suppose that there are reasons for abstaining from mentioning them. With organic colouring matters, too, it is hard to see how molecular change can be avoided, although, as a temperature of 100° C. is not exceeded, its effects might be hardly perceptible.

Finally one circumstance of theoretical importance must be mentioned. This is that solid bodies are better conductors of heat than fluids. It is therefore certain that when accompanied by such large quantities of solid as the inventor uses, the oil would be heated much more rapidly and uniformly than if heated by itself. Whether this might not change the vehicle itself may well be doubted. But with the special circumstances which must be maintained during the process, we have no direct evidence that such is the case.

We stand then face to face with an invention which we should wish to be a step forward in paint manufacture. But to be able to judge of it rightly we were obliged to experi-

ment, and we have entered upon an accurate investigation, the results of which are here briefly described.

1. *Experiments with Pure Linseed Oil.*—As the specification does not exclude the use of pure linseed oil in paint manufacture, we began our researches with that substance. To be quite sure of our ground we used no bleached oil, as that substance may contain impurities resulting from its manufacture which would have had a bad effect.

The oil we used was a perfectly natural, beautifully clear, and old-stocked sample.

In the manner directed by the inventor, 1. pure zinc white, 2. pure ochre, 3. chrome yellow, were rubbed up with the oil in the proportions of 6 vols. pigment to 1 vol. linseed oil.

The mixtures were put into suitable porcelain dishes and weighed. For the purposes of comparison and to see what effect the increase of temperature produces, some of the oil and some of the pigment were heated, each by itself, on the same sand-bath. The temperature was raised gradually and steadily. At 120° C. a few bubbles of gas were disengaged, and the mixtures became thicker, but not tough or brittle. The heating was continued with constant stirring. The mixture then turned liquid again, and remained so till the end of the two hours demanded by the specification. The dishes were then removed from the bath and rapidly cooled. Their contents could then be used without any more oil.

It was interesting to note if the heating had caused any loss, indicating decomposition. When, however, the dishes were weighed it was found that the pure linseed oil had lost ·02 per cent. of its weight, the ochre mixture ·05 per cent., and the zinc white mixture ·03 per cent. These quantities are quite insignificant and afford no ground for assuming any marked decomposition (the chrome yellow dish had spurted over, so that it had to be left out of the reckoning).

Neither the linseed oil nor the mixtures were much changed

in colour by the heat. In fact it was difficult to tell the heated from the unheated. The pigments heated by themselves were just a trifle darker.

The masses obtained by this treatment did not dry as rapidly as might have been expected. The mixtures painted on glass took nearly five days to dry. The glass plates lay in a room only slightly heated, and the weather was wet and cold. The comparison sample made of ordinary linseed oil took about the same time, so that no noticeable advantage existed.

2. *Experiments with Boiled Oil.*—We convinced ourselves that the material used was quite pure. Its colour was a pale yellow.

It was rubbed up with, 1. zinc white, 2. ochre, 3. chrome yellow, in the proportion of 5 vols. pigment to 1 vol. oil.

The mixtures were heated on a sand-bath in porcelain dishes, as above, and some of each of the pigments and some of the boiled oil were heated separately on the same bath with the mixtures.

The temperature was raised with great care and steadiness, and with constant stirring. As in the other experiments the masses became thick between 120 and 160° C., but only the ochre appeared friable. As before a few gas bubbles appeared; but there were perceptible changes in the appearance of the mixtures. The zinc-white mixture became paler, and the chrome yellow one much darker. The ochre mixture, however, hardly changed at all. At the end of the two hours' treatment and stirring, the dishes were rapidly cooled and the drying properties at once tested.

It must be mentioned that subsequent grinding diminished the change in colour suffered by the zinc white and the chrome yellow, but did not bring them back to the purity of colour possessed before heating. No difference was perceptible in the case of the ochre.

The products painted very well, but did not dry so quickly

as the inventor claims. The zinc-white mixture took five days to dry, the ochre mixture four days, the chrome yellow mixture four and a half days. In any case they have no advantage as regards drying over ordinary good oil paint. Some pigments, in fact, painted on at the same time were dry sooner. Whether the pigments prepared by the patent process are more durable than others time, of course, can alone decide.

From these experiments we may conclude that the chief advantage in the patent process must consist in economy of vehicle, and that it will give good oil paints with pure and dry materials of good quality. If 40 per cent. of oil is really saved cannot be ascertained, as we had none of the paints prepared by the inventor to analyse.

Mussini Paints.

These are a new sort of artists' oil colours invented by Professor Cesare Mussini, and put on the market by Schminke & Co. of Dusseldorf. They may be considered, according to Horadan's report of 18th February, 1887, to the German Society for the Promotion of Rational Painting, as ethereal resin oil colours. If the name Mussini is retained it will be in honour of a man whose knowledge of the qualities necessary in fine paints has enabled him to establish a principle highly favourable to the users. The Mussini colours have the eminent advantage over ordinary "novelties" in the fact that they have been tested by the existence of pictures painted with them fifty years ago. In 1873 the Russian artist Airasowsky wrote how splendidly the pictures painted in St. Isaac's Cathedral at St. Petersburg by Mussini in 1843 to 1846 had lasted in comparison with others painted at the same time with ordinary oil paints. These pictures still remain in all their original freshness and clearness. The Florentine Academy also testifies to the excellent preservation of some large pictures which Mussini painted on a lime ground

in Florence. Von Olfers of Berlin testifies to an extremely convincing proof of the durability of the Mussini colours. When Mussini travelled from Berlin to St. Petersburg, in 1846, one brick was painted with ordinary oil paint, another with fresco, and a third with Mussini colours. The three were put together on to the roof of the museum. When Mussini came back two years afterwards, the bricks were examined. The exposure to the weather had entirely destroyed the applications to the first two bricks, but the Mussini colours on the third brick were unchanged.

Mussini colours have three chief differences from ordinary poppy oil paints.

1. Each paint is treated with regard to its own special nature, and contains only as much fatty oil as is absolutely indispensable to bind it. The rest of the vehicle consists of ethereal oils, which give the necessary thinness.

2. Every colour contains a certain amount of resin proportioned to the oil also put with the pigment.

The paints dry uniformly. They quickly become plastic, and then dry from within outwards, *i.e.*, in the exact reverse way to ordinary oil paints. With these a skin forms on the outside, and the inside remains moist for a long time.

The following analyses show the differences between Mussini and ordinary paints with reference to the amount of oil in them:—

Pigment.	Percentage of oil usually.	Percentage of oil in Mussini paint.
White lead	12	8
Chrome yellow . . .	19	10
Ochre	75	33
Cassel brown	75	40
Cobalt blue	125	60
Sienna earth	131	80

The rest of the vehicle is an essential oil, which evaporates and makes the paint dry very clear.

Mussini called the vehicle of his paints sugo (from *sugare*, to dry). What the fatty oil in it is, and what the resin is

(soft resins should make the paint dry uniformly) Horadan does not say, because he is bound to silence, but nut oil is not far from the mark, and is much more suitable for the purpose than either linseed or poppy oil.

The preparation of Mussini colours varies according to their intended use. One description is prepared for picture painting; another for wall decoration.

They offer no difficulties in use for easel-painting, but on the contrary much facilitate it. They can be applied to wood, stone, metal, paper, in short to any solid surface without any fear that the colour will come off, as Mussini colours adhere much better than ordinary oil-paints. The surface to be painted should first be well rubbed over with medium, which increases the adhesion of the paint. The characteristic method of drying of the Mussini paints has special advantages. Effects can be produced from the first which are unattainable with ordinary oil paints. A specially important property in picture painting is that every coat sets at once, so that no colour runs, and it is possible to paint on a new coat over the first in a very short time.

The Normal Pigments of the German Society for the Promotion of Rational Painting.

This society, wishing to free the market from the many non-durable pigments which many makers offer to artists, to the injury of the artists and of art, has founded an institution for testing pigments and vehicles, and permits every manufacturer who offers the necessary guarantees and who will conform to the conditions to be presently stated to sell his products as "normal colours of the German Society for the Promotion of Rational Painting".

These conditions are:—

1. Every manufacturer wishing to sell his goods under the above title must send notice to the society and at the same

time samples of his pigments to the testing station of the society.

2. The testing station having examined the pigments, the manufacturer may be called upon to make a first and only payment to the station of M. 100.

3. The manufacturer must bind himself always to use for his colours the same pigments as he has sent to the testing station and which have been there approved, and, when he has begun business, to send two sets of filled tubes to the society.

4. Permission to use the title will not be given until the raw materials have been approved by the testing station and will emanate from the committee of the society.

5. The control is continuous, and the permission will be withdrawn if the manufacturer alters the composition of his paints without notice to the society, or does not make them of the same quality as before.

6. The title will only extend to substances included in the list of the committee. (This has been already given, see p. 165.)

7. The normal-colours must be labelled according to the following form:—

1.	Normal Paint of the German Society for the Promotion of Rational Painting.
2.	Finest prepared oil paint.
3.	Light ochre. Ocre clair.
4.	Louis Edgar Andes, Vienna.

No. 1 must be exactly as set forth. No. 2 is filled up by

the manufacturer, and shows how the paint is made, *i.e.*, whether it is an oil paint, an oil-wax paint, or resin paint or prepared after Mussini or Keim, etc.

No. 3 gives the name of the paint as determined by the society, and both in German and French. It is specially important that there should be uniformity of terminology.

No. 4 gives the name of the manufacturer, and is filled up as he chooses.

8. The control over the normal paints is confined to the pigments. It does not extend to the vehicles, as at present no standard for these can be fixed. The fixing of such a standard is however kept in sight. Nevertheless the committee considers it desirable that the oil present should be named, and it recommends the adoption of vehicles free from lead.

The general method of testing the normal paints is as follows:—

(*a*) The pigment is subjected to a complete qualitative and quantitative analysis, carried out if possible by specialists, to get an accurate idea of its composition.

(*b*) The pigment undergoes a special microscopic examination.

(*c*) To ascertain accurately all the chemical, physical, and optical characters considered important as regards the use of the pigment, it is subjected to the action of—

1. The air.
2. Sunlight or electric light, both dried and diffused.
3. Atmospheric agencies, *e.g.*, rain, frost, snow, etc.
4. Acids and alkalies.
5. A red heat and
6. Various vehicles.

The tests of exposure to light and air are carried out both with and without vehicle, in the following manner, so as to get accurate results.

Tests with the Powdered Pigment.—The pigment is powdered

so as to go through a sieve with about 500 meshes to the square centimetre, and then exposed both in open and closed glasses, some samples to direct, some to diffuse light, while others are kept in the dark, and the various changes are noted.

Tests with the Pigment Rubbed up with Vehicle.—The rubbed pigment is exposed to the same series of tests as above, being painted on ground glass, the most inactive basis that can be found.

Each sample is divided into three, one being left unvarnished, another varnished with a solution of pure mastic in oil of turpentine, and the third both varnished and covered air-tight with a glass plate cemented over it. The paint is varnished as soon as it ceases to be sticky, and the glass plate is laid on as soon as the varnish is dry.

The vehicles used in the tests are :—

1. Purified unbleached linseed oil.
2. Purified unbleached poppy oil.
3. As a water-soluble vehicle, gelatine.
4. As a strong alkaline vehicle, waterglass.

In all tests the proportion between vehicle and pigment is accurately recorded.

The pigment to be tested is well washed, dried at 100° C. until its weight is constant, and used when cold Wherever possible full particulars of the time when and the place whence the pigment was received are to be recorded.

Finally it is to be remarked that we are not to understand that normal paints are new paints or paints made by particular makers, but that only long known, durable, and pure pigments can have a claim to the title, and those whose composition is known to the society and is controlled by it, and which therefore the artist can accept and use as normal paints guaranteed as to purity. The same name will then always mean exactly the same pigment.

Cotton Seed Oil, and Its Detection in Oil Paints, Particularly in Artists' Colours.

Dr. Hans Stockmeier of Nuremberg has instituted tests of a number of artists' colours to see whether they were really made of pure linseed or poppy oil, and has established beyond the possibility of doubt that no small part of the artists' oil-colours sold are made with cotton oil, which is at present decidedly cheaper than either poppy or linseed.

Dr. Stockmeier tested the following paints:—

1. Permanent flake white, from a London firm.
2. Light red, from Winsor and Newton, of London.
3. Burnt sienna, from Dr. Schonfield & Co., of Dusseldorf.
4. Chinese ochre, from G. B. Moeves, of Berlin.
5. Brown red, a sketching colour from Schminke & Co., of Dusseldorf.

The five tube-colours were first extracted in weighed quantities and in closed vessels with ether in four separate portions. The collective ethereal extract from each was evaporated down on the waterbath, and the remaining oil was then dissolved in petroleum ether. The petroleum ether was then distilled off and the residual oil was weighed. The results were as follows:—

1.	44·078	grammes	gave	7·152	grammes	oil	= 16·23	per cent.
2.	8·1845	,,	,,	3·429	,,	,,	= 41·89	,, ,,
3.	19·8925	,,	,,	11·769	,,	,,	= 59·16	,, ,,
4.	13·286	,,	,,	5·9923	,,	,,	= 45·1	,, ,,
5.	35·233	,,	,,	10·9632	,,	,,	= 31·11	,, ,,

The oil from—

1. Was thin, nearly colourless, with a yellow tinge.
2. Thin and yellowish.
3. Thick, nearly colourless, with a yellow tinge.
4. Thick and yellowish.
5. Butter-like in consistency and yellow.

Each oil was now tested by Hübl's iodine method as follows: A known weight of the oil was weighed out, dissolved in chloroform, and then left for two hours in a closed vessel

with an accurately measured volume of solution of mercury iodo-chloride. Then water and a 10 per cent. solution of potassium iodide were added, the solution was bleached with sodium thiosulphate and then titrated back with 1 per cent. starch paste and the mercury iodo-chloride, till a blue colour appeared. The strength of the iodine solution was accurately known, and 10 c.c. of it corresponded to 8·34 c.c. of the solution of thiosulphate. The strength of the latter was got with sublimed iodine as 26·738 grammes iodine per litre. Two tests were made with each sample.

Sample.	Oil used. Grammes.	c.c. of Mercury Iodo-chloride used.	c.c. of Sodium Thiosulphate used.	Iodine No. hence Calculated.	Average Value of Iodine No.
1 (a)	·4727	32·2	5·4	121·6	122
1 (b)	·393	31·4	8·2	122·4	
2 (a)	·222	20·6	4·6	151·7	151·4
2 (b)	·3594	21·6	6·1	151·0	
3 (a)	·3775	31·1	9·4	116·9	116·8
3 (b)	·2291	20·5	7·1	116·7	
4 (a)	·451	31·1	9·2	99·1	99·5
4 (b)	·3081	20·9	5·9	99·8	
5 (a)	·531	41·4	15·1	97·7	98·2
5 (b)	·2657	29·9	7·5	98·6	

When the iodine numbers had thus been obtained, the fusion and solidifying points of the fatty acids present were determined.

For this purpose a sample of each oil was boiled with alcoholic potash, and the soap was decomposed with hydrochloric acid. The following table describes the fatty acids:—

Sample.	Fusion Point Deg. C.	Solidifying Point Deg. C.	Remarks.
1	22	Partly solidified at 18	
2	—	Did not solidify at ordinary temperatures	The acid was a blood red.
3	28	24	
4	35	32	
5	35	30	

These high fusion points created a presumption that cotton oil was present in Nos. 1, 3, 4 and 5, and no other oil in 4 and 5, and that linseed oil was also present in Nos. 1 and 3. The iodine number and general behaviour of the fatty acid of No. 2 showed that the paint was made with linseed oil only.

Further special tests were made from cotton oil and checked by control tests made with a sample of pure cotton oil.

The elaidine test with nitric acid and copper gave a negative result at first with all the samples, but after two days pure cotton oil, and Nos. 4 and 5 were ointment-like, Nos. 1 and 3 partly so. No. 2 remained liquid.

On treatment with nitric acid of sp. gr. 1·33 the following results were obtained:—

Sample.	Action in the Cold.	Action on the Water-bath.
Cotton oil.	Yellowish brown.	Brownish red } Action vigorous.
1.	Brownish.	,, ,, }
2.	Pale yellow.	Yellow.
3.	Yellowish brown.	Red
4.	,, ,,	Brownish red } Action vigorous.
5.	,, ,,	,, ,, }

After eighteen hours all the samples had an ointment-like consistency.

These results confirm the former conclusions as to the nature of the vehicle.

Further tests for resins, paraffin and resin oils gave negative results. For the presence of resins the full solubility of the oils in petroleum is partial evidence.

The results obtained also show that the cotton oil present had been boiled and in every case bleached afterwards. This is shown by the low iodine number (that of raw cotton oil is 105 to 108), and the strong acid reaction of the ethereal solution observed, especially with Nos. 4 and 5, and finally by the ointment-like consistency produced by the presence

of free acid shown at the ordinary temperature by the oil from No. 5.

Boiled cotton oil is about on a par with poppy oil as regards drying, and the cotton oil is evidently intended as a substitute for the dearer poppy oil. The linseed oil in No. 2 has also evidently been boiled or at least was a mixture of boiled and unboiled oil. This is the more probable supposition. Here, too, the low iodine number is a sufficient indication, and also the blood-red colour of the fatty acid. This colour points to the presence of a large proportion of linoxic acid.

Pure linseed oil has an iodine number of 156 to 160, with a mean of 158. Von Hübl found that of boiled linseed oil to be 148.

If we sum up our results, we find that

No. 1 has a vehicle consisting of 72 per cent. cotton oil and 28 per cent. linseed oil.

No. 2 was prepared with linseed oil alone. Here we cannot lay much stress on the iodine number, 148, for boiled oil, which can only be accepted with great reserve, as further determinations of it are necessary. But we may say, with this reservation, that the vehicle consisted of 66 per cent. boiled and 34 per cent. unboiled linseed oil.

In No. 3 the oil was a mixture of 82·4 per cent. of cotton oil and 17·6 per cent. of linseed oil.

In Nos. 4 and 5 it was cotton oil only.

We are now met by the question how far the artist is injured by the most inferior of these products, whether, that is, such a composition of the paint will have any adverse influence on the properties for which it is valued in picture painting, namely, beauty and durability. There is no positive experience to be appealed to in this matter, but it behoves the manufacturer to abstain from using vehicles of which the effects are unknown.

These results are also here stated to show how widely the tendency to use cheaper oils has penetrated into the trade.

CHAPTER XXII.

PRINTERS' INKS: VEHICLES.

PRINTERS' inks may be divided into two great groups: Black printing inks; Coloured printing inks.

This classification is, of course, obvious.

Both classes consist of vehicle and pigment. The same vehicle may be used for either kind, but the pigments are necessarily different, and while with black ink we have to do with lampblack, an extremely light pigment, we find for coloured inks many heavy ones used, such as lead, mercury and chrome compounds.

Far more black than coloured ink is used, and we shall consider it first after discussing the vehicle used for both kinds.

The vehicle being one of the two essential ingredients of a printers' ink must, of course, be made of faultless quality before a good ink can be got from it. The properties which the ink itself must have must be kept in view in the manufacture of the vehicle. These I now give, and will follow them with a recapitulation of the properties which the vehicle must have in consequence.

A good printing ink must—

1. Have a perfectly uniform syrupy consistency, and if black must be of a shining blue black, not a grey black. No lumps of pigment must be discoverable in it, or any other impurities.

2. It must come freely off the rollers and on to the type in the machine.

3. Its colour must be pure. It must not smudge the types, and must be easily washed off them.

4. It must dry neither too fast nor too slowly. If it dries too slowly, it hinders moving and folding the sheets, which would be very awkward in printing a daily paper. If it dries too fast, it would set on the types, during printing, and make the paper stick to them and tear, and so stop the press. It would also tear pieces out of the inking rollers, which would get on to the types.

5. The ink when dry must not set off on to another sheet, or else two printed sides which had come together would become illegible, and it would also dirty the hands of readers, a circumstance which has caused trouble to newspaper owners before now.

6. The ink must have no strong smell, or if it has the smell must vanish when the ink is dry.

7. The ink must not leave greasy margins round the letters when it is dry. This is specially important in book printing, but is to be avoided in newspaper work, although newspapers are printed and read to-day, and thrown away to-morrow.

From these we deduce the following requirements for the vehicle:—

1. It must be of perfectly uniform consistency, without any bits of film, or solid lumps of any kind. It must be filtered after it is made and kept in clean and well-closed vessels, so that no dust or dirt can get at it.

2. It must be tough but not sticky from resin mixed with it.

3. It must not be too weak, or the printing will smudge, and compositions which contain resin, resin oil, paraffin oil, etc., are very difficult to dissolve in printers' lye, so that the formes are difficult to clean when they are used.

4. It must take the right time to dry, but the oxidising agents used in making ordinary boiled oil for paints must not be used in its manufacture.

5. It must have the necessary power of binding the lamp-black or other pigment.

6. It must have no disagreeable smell. When linseed oil and resin are used in making it, the smell is never unpleasant, but with resin oil or paraffin oil, additions which cannot always be avoided for reasons of price, the case is otherwise.

7. All unbound oil must be avoided, so that all linseed oil must be boiled thick, for such oil gives no greasy border round the letters.

A vehicle consisting only of linseed oil answers all these requirements, and they must not be expected too strictly from those containing resin, coal-tar, paraffin or resin oil, etc.

Linseed oil at a temperature of 380° to 400° C., *i.e.*, when it may be expected to catch fire every moment, changes to a thick, tough, sticky mass, which makes no greasy mark on paper either by itself or when mixed with pigment. By regulating the duration of this high temperature we are able to govern the thickness of the oil, and can even by long boiling get a perfectly solid mass which will not yield to the pressure of the finger.

No oxidising agents may be added to accelerate the manufacture of a vehicle intended for printing ink, because they produce the stickiness which we have said must be avoided, and because oil boiled with lead or manganese compounds alters for the worse when kept.

According to the thickness required the oil is boiled for a longer or shorter time. The practice formerly universal and considered essential, of setting fire to the linseed oil, is not followed now in any well-managed factory, as it darkens the oil very much, and that makes it unsuitable for coloured inks of light tints, although it does not matter for black ones.

The demand for cheap ink, especially for newspaper printing, has led to attempts to get rid of thick boiled linseed oil in favour of cheaper materials, such as resin oil, resin, paraffin oil, coal-tar, turpentine and soap. With these we get composition vehicles, and they have already been brought to such perfection that practically all newspaper ink is made

with them. For better class printing, however, they have not yet been made suitable. For that we have still to restrict ourselves to a vehicle of boiled linseed oil only.

Any strong and heat-resisting vessel will serve for this

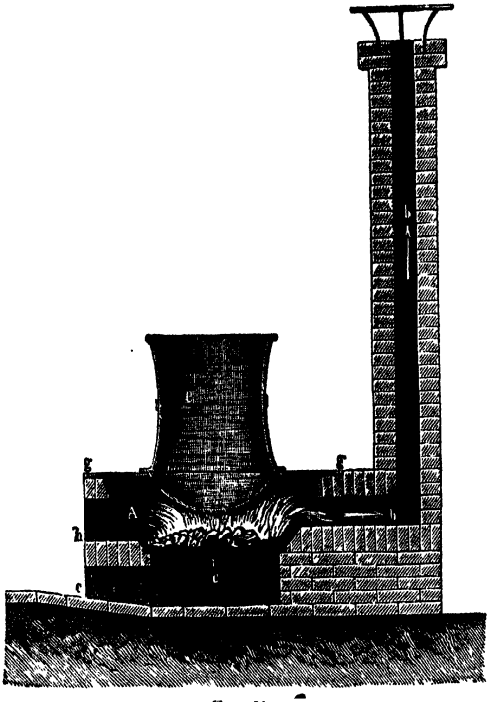


FIG. 55.

manufacture, and no particular shape is indicated. Iron or copper is the best material.

In former times pear-shaped vessels with narrow mouths were used, made of iron or copper, but this shape has been entirely discarded and vessels are used which are deeper than they are wide. Experience has shown that there is a bulk

above which the oil becomes unmanageable, and it is therefore advisable not to use vessels holding over 100 kilos., even with mechanical appliances for lifting them, while in the absence of such, the capacity of the vessel should in no case exceed 30 kilos. or 40 at the most. Enamelled cast-iron is an excellent material for these vessels, while copper, which is very apt to oxidise and turn the oil green, is to be avoided.

I use for boiling the arrangement shown in fig. 55. It consists of a brickwork fireplace, ashpit, and flues, an iron grate, and a plate of iron 2 cm. thick with a circular hole in the middle of it to receive the oil kettle. The brickwork hearth is a square of about 1½ metre wide, and about a foot high. The kettle, of enamelled cast-iron, is of the same diameter at top and bottom, but somewhat contracted in the centre and with a concave bottom. Its height is 65 cm. and its width about 45, and it holds if filled to the brim between 50 and 60 kilos. of oil. For lifting the kettle there are two wrought-iron rods, 2 to 3 metres long, which are passed through rings attached to the sides of the kettle. This enables the workmen carrying the kettle to be at some little distance from it, which is very necessary in case of the oil catching fire. An iron stand or tripod is provided to take the kettle when it is off the fire. As can be clearly seen from the figure the kettle is heated at the bottom only, but that is quite enough to raise the contents to the high temperature necessary. To keep up the fire charcoal, coal, or coke is used.

Andres' Boiling Apparatus.

Andres has invented a very pretty apparatus which is shown in fig. 56.

It consists of a cylinder C of sheet copper. Half-way up it is surrounded by an annular basin R. The mouth of the cylinder is surrounded by a strong iron ring to which the chains K of a tackle are fixed, whereby the cylinder can be

quickly lifted out of the fire. There is also a cover. D which fits nearly air-tight on to the mouth of the cylinder. The whole apparatus should stand under a brick arch as a safe-guard against fire. This arch should have an opening above into a chimney with a good draught, to get rid of the fumes from the hot oil. The attendant must have a stool high enough to let him get samples out of the cylinder. An

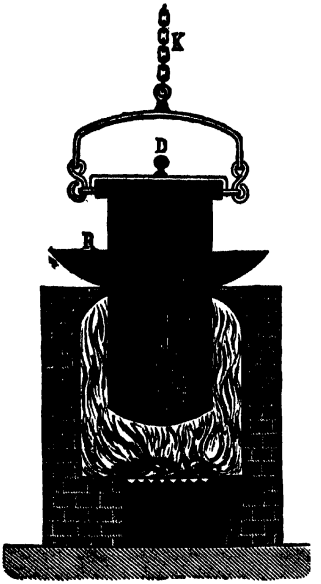


FIG. 56.

apprentice has charge of the crane, to lift the cylinder and move it to one side when ordered.

Other arrangements of this apparatus are also made; one is to put the cylinder in a carrier on rails, as a substitute for the crane, so that the cylinder can easily be put over or off the fire as may be required, or even into the open air, where it may be left to cool.

In the factory of Kast and Ehinger, of Feuerbach-Stuttgart, the following precautions are taken to prevent accidents arising from the oil boiling over. In one apparatus, the kettle is supported on a frame running on wheels on rails, so that, when an iron door in the walled-up hearth is opened, a single man can quickly remove it from over the fire. The other arrangement is to make the fire movable instead of the kettle. The firegrate consists of a wheeled carriage running on rails, so that it can be easily moved from under the kettle. To get less energetic heating, and to save labour, brown coal is used for fuel instead of ordinary coal.

Boiling Process.

The process of boiling is as follows: When the kettle has been filled about two-thirds full with good long-stocked pure linseed oil, it is brought over the fire, or the fire is brought under it, and it is heated till it begins to froth. Then the fire is increased. When a temperature of 230° to 250° C. is reached, as is shown by the oil changing colour almost suddenly and becoming a pale greenish yellow, the firing is managed so as to keep it at that temperature for about half an hour, and it is then increased again. The oil now begins to fume strongly with evolution of acrolein, and presently, say in from one and a half to two hours from the start, begins to froth again. Care is necessary, for the oil is near that temperature when it catches fire, and if it froths very much it is best to stop the heating for a time. Now the thickening of the oils begins and the temperature is kept constant as it thickens. The fumes and the acrolein-smell continually increase, and the danger of the oil igniting spontaneously is always present.

If it does so, with a slight report, the flame is easily put out with a damp, not dripping, cloth and a cover, but both must be at once removed, and one must be prepared to use them again as required. This method of treatment has how-

ever the drawback that it confines the continually increasing vapours, as there is no rapid cooling, and it is a better plan to put out the flame with a wire grating. A thick wire grating on a handle will at once extinguish the flame without confining the fumes. If strong frothing occurs before or after the oil catches fire, cold oil is added, or better some cold already boiled oil, which will not check the incipient thickening.

The progress of the thickening must be tested by taking samples from time to time. These samples are taken with a spatula and rapidly cooled on an iron plate. The length of the threads into which the cooled oil can be drawn and its adhesiveness are the signs. It is possible to push the heating so far as to get a solid elastic non-adhesive substance, the so-called oil-caoutchouc, which however does not concern us.

It goes without saying that with an open fire which does not allow change of temperature to be made regularly, or a uniform temperature to be maintained, a boiling process regular under all circumstances is an impossibility, so that no times can be stated as required for getting any given thickness of the oil: hence the necessity for testing samples at intervals, to determine whether the oil wants more heating or not. Another cause of this necessity is differences in the oils treated.

To get exact standards for the thickness of an oil, it is best to use the hydrometer, and then by mixing different boilings in the proper proportions we can always obtain exactly any given thickness required.

No addition of any kind, driers, resin, etc., should be added if the vehicle is to be used or sold as a pure linseed oil. It is a question of giving the oil the necessary thickness to hold the pigment and to lose the property of making greasy stains. The process above described is necessarily dangerous and tedious, so that for a long time other materials have been

used, which have not those drawbacks, it is true, but which only give a proper vehicle for certain purposes in the printing trade. Among these are: (1) Boiled linseed oil and resin; (2) boiled linseed oil, resin, and resin oil; (3) raw linseed oil, resin and resin oil; and (4) composition vehicles.

Vehicles of Linseed Oil and Resin.

The basis of these is thick boiled linseed oil, prepared as above described. The oil, however, is only boiled till it will not grease paper. The thickness then wanting is given by the addition of resin, so that a cheaper ink may be made with the vehicle. When the oil has been boiled it is left to clear for a short time, and then reheated to receive the resin, which must be as dry as possible, and broken into small pieces. These pieces are fused over a gentle fire and then mixed first with some resin soap cut up, and when that has dissolved with the hot oil. The mass is constantly stirred, left for half an hour on the fire till it is very thin, and then filtered through a linen cloth to stop all the impurities of the resin. The finished vehicle is allowed to deposit all particles too fine to be stopped by the cloth, and after a few days is drawn off from the sediment.

The following recipes can be varied according to requirements. Larger quantities of boiled oil can only improve the quality of the vehicle by making it stronger and smoother and forming a better ink. The numbers mean kilos in all cases.

	Thin.	Medium.	Thick.
Resin	25	25	25
Boiled linseed oil	100	100	100
Resin soap	8	8	8
Weak boiled oil	7	4	—
Resin	50	50	50
Boiled linseed oil	100	100	100
Resin soap	10	10	10
Weak boiled oil	9	6	—

	Thin.	Medium.	Thick.
Resin	77	77	77
Boiled linseed oil	100	100	100
Resin soap	7	7	7
Weak boiled oil	12	9	—

Resin Oil Vehicles.

The use of resin oil for this purpose was first proposed in 1878 by Pratt of New York. His formula is

	Kilos.
Resin oil	20
Resin	8
Yellow soap	2

amalgamated by heat. If the mass is to be thicker, the soap and resin are increased, and *vice versa*. A later recipe is

	Kilos.
Resin oil	50
Resin	39
White soap	9

amalgamated by heat with constant stirring till the mixture is quite perfect. The thickness is regulated by increasing the amount of soap and resin, or that of the oil.

Resin oil first began to be largely used for this purpose in 1860, when the progress of the resin industry enabled it to be more generally employed by producing resin oil of a less penetrating odour than was before possible. Newspaper inks are now made from resin-oil vehicles almost exclusively, although the public often complain about the smell.

In the manufacture, the resin and the resin oil are heated together, the soap being added later. Finally boiled linseed oil is added and the whole is kept for a few hours at 120° to 140° C., to get rid of the smell of the resin oil, and to obtain a perfect mixture of the ingredients. In the following recipes the quantities are in kilos.

1. Thin vehicles with boiled linseed oil.

	Thin boiled linseed oil	Resin soap	Boiled linseed oil	Resin oil	Resin
(*a*)	7	3	50	50	25
(*b*)	9	5	50	50	50
(*c*)	12	7	50	50	75

2. Medium vehicles with boiled linseed oil.

	Thin boiled linseed oil	Resin soap	Boiled linseed oil	Resin oil	Resin
(*a*)	4	3	50	50	25
(*b*)	6	5	50	50	50
(*c*)	9	7	50	50	50

3. Thick vehicles with boiled linseed oil.

	Resin soap	Boiled linseed oil	Resin oil	Resin
(*a*)	3	50	50	25
(*b*)	5	50	50	50
(*c*)	7	50	50	75

4. Thin vehicles with raw linseed oil.

	Resin	Thick turpentine	Resin soap	Linseed oil	Resin oil	Raw linseed oil
(*a*)	—	2	2	52	96	84
(*b*)	100	—	7	85	95	—

5. Medium vehicles with raw linseed oil.

	Resin	Resin soap	Thick turpentine	Linseed oil	Resin oil	Linseed oil
(*a*)	—	5	5	1050	240	210
(*b*)	100	70	—	3500	80	—

6. Thick vehicles with raw linseed oil.

	Resin	Resin soap	Thick turpentine	Linseed oil	Resin oil	Linseed oil
(*a*)	—	5	5	87	240	210
(*b*)	100	7	—	25	80	—

Composition Vehicles.

For Fine Work.—1. Copaiva balsam, 70 kilos.; ordinary linseed oil, 50 kilos.; colophony, 110 kilos.; almond benjamin 3 kilos.; Tolu balsam, 2 kilos.

2. Copaiva balsam, 85 kilos.; ordinary linseed oil, 40 kilos. colophony, 115 kilos.; almond benjamin, 3 kilos.; Tolu balsam, 2 kilos.

Goyneau's Recipe.—1. Linseed oil, 979 parts; resin, 735 parts; syrup, 245 kilos.; litharge, 125 kilos.

2. Linseed oil, 400 kilos.; resin, 380 kilos.; syrup, 490 kilos.; litharge, 60 kilos.

3. Linseed oil, 980 kilos.; resin, 958 kilos.; syrup, 980 kilos.; litharge, 122 kilos.

The oil is mixed with the litharge, while a slow fire is kept up under the kettle, until the oil begins to swell and to show a froth. In the meantime the resin is melted with a little linseed oil, and added to the oil when the latter has ceased to froth. Then the mass is well stirred, and when it has somewhat cooled the syrup is added.

Savage's Recipe.—32 kilos. of copaiva balsam are mixed with 12 kilos. of resin soap.

Knecht's Recipe.—5 kilos. of Venice turpentine, 15 kilos. of castor oil, and 1 kilo. of white wax are mixed well together over the waterbath.

Rösl's Recipe.—9 kilos. thick turpentine, 10 kilos. of soft soap, and 4 kilos. of oleine are mixed together hot.

Resin Soap Vehicle for Gold Printing.—This composition consists of a solution of resin soap with glue and glycerine. It is made as follows:—

We dissolve 50 kilos. of soda in 150 kilos. of water in a copper kettle, and raise it to the boil. We then gradually add with continual stirring 100 kilos. of powdered colophony, and then keep up the boiling for two or three hours, or at least until the liquid becomes clear and quite transparent. We then allow the liquid to cool, and pour it off from the tough brown resin lying at the bottom. We then add 100 kilos. and 15 kilos. of soaked glue and heat up till everything is dissolved. The vehicle thus prepared dries quickly. If it is wanted to dry slowly, it is additioned with from 10 to 20 kilos. of glycerine of 28° B.

Thenius's Recipe.—Take 25 kilos. linseed oil, 3 kilos. of fine litharge, and boil until the linseed oil, on cooling, begins

to get thick, and then allow to settle. In the meantime melt 10 kilos. of pale American resin, and add it to the oil, and boil for a time longer. Finally add 5 kilos. of coal-tar varnish, heat again for a time, and stir till cold. The vehicle must be thick and of the consistency of honey.

CHAPTER XXIII.

PRINTERS' INKS: PIGMENTS AND MANUFACTURE.

As we have already said, black printers' ink consists of vehicle and lampblack. When you see the statement in a book that it is difficult to say exactly the proper constitution of printers' ink, you may be sure that the author is a cautious man. Here we shall give precise directions.

We have now to get our product to mix together vehicle and lampblack, a process which was carried out at the beginning of the printing art, just as it is now, except that the rubbing together is now done by machinery of the best construction.

On account of the great toughness of the vehicle and the great lightness of the lampblack, the mixing of the two is best done in a closed mixing machine, such as those described earlier in this book. The rubbing up in the machine must be very perfect to get a faultless product, such as those of Lehmann and others. The finished ink must contain no lumps of any kind, and it must have the finest ointment-like and uniform consistency, as is only possible with the above-named machines, whose suitability for printers' ink has been already mentioned.

The proportion between lampblack and vehicle is various, and depends chiefly on the nature and origin of the pigment. In general, the finer the lampblack, the less of it is required to make a good printing and good covering ink, for the fine lampblack always goes farther. The proportion varies from 21 to 40 parts of lampblack to 100 parts of vehicle, whether the ink is to be thin, medium or thick. The quantity of lamp-

black cannot affect the thickness of the ink, which depends mainly on the consistency of the vehicle used. Unfortunately, manufacturers fall over this wrong notion occasionally that they can make a thick ink by putting a lot of lampblack to a thin vehicle, and then discover when too late that their ink is unusable.

As an ink with a certain blue-black colour and lustre is required for fine illustrations and sumptuous painting, and this cannot be got with lampblack alone, these inks also contain Prussian blue or indigo, or aniline dyes which have been already used with success. Prussian blue and indigo being hard pigments, must be subjected to a preliminary treatment to enable them to be rubbed up more easily. This consists in soaking them for a day or two in 96 per cent. spirit, then grinding them, and finally spreading them out to allow the alcohol to evaporate. Aniline dyes, principally blue and violet, must be soluble in oil, so as to dissolve in the varnish without leaving any residue.

As already mentioned, the proportion of lampblack in the ink depends upon the nature of the former, so the recipes now about to be given for making printers' ink cannot be regarded as correct in all cases, but must be taken as subject to many modifications.

Inks for Rotary Machines.

	Thin.	Medium.	Thick.
1. Vehicle	70	72	72
Lampblack	30	28	28
2. Vehicle	72	74	74
Lampblack	28	26	26

Inks for Rapid Printing.

Newspaper Inks.

	Thin.	Medium.
Vehicle	78	76
Lampblack	22	24

Book Inks.

	Thin.	Medium.	Thick.
Vehicle	77	79	80
Lampblack	23	21	20

Illustration Inks.

	Thin.	Medium	Thick.
Vehicle	78	78	78
Lampblack	20	19	19
Prussian blue	2	2	1
Indigo	—	1	—
Steel blue	—	—	2

As we have seen, the vehicle in all the inks is on an unchanged basis. It is therefore evident that it is on the quality of the lampblack that the beauty and value of the ink chiefly depends. It is impossible to incorporate the pigment with anything better than the proper amount of pure oil vehicle, and this shows that all inks would be of the same quality if there were no differences in the quality of the lampblack, which has the chief influence on the nature of the ink. Hence in order to make a newspaper ink at a medium price we must use a common lampblack made from tar or paraffin, or in some cases from resin, while better lampblack is used for book-work, and for illustrations the lampblack is calcined several times. For these reasons it is difficult to give formulæ, and in what follows I will only indicate the usual proportion. The true formulæ can be arrived at only by practice.

Brackenbusch's Improvements.

The object of this inventor is to replace the linseed oil vehicle now used in printing-ink manufacture, either altogether or with such additions as are required either to lower the price or to give some special lustre. These substitutes are mixtures of the heavy hydrocarbons and resins, and these are cheaper, dry quicker, and give more uniform inks.

Consistent Black Printers' Ink.—25 parts of paraffin oil and 45 of fine colophony are mixed either by melting the resin

at about 80° C., or by mechanical grinding at the ordinary temperature. The mass then receives a further addition of 15 parts of lampblack.

Soft Ink for Rotary Machines.—In place of the 45 parts of fine colophony take 40 only. With this exception the process is the same as the last.

Jobbing Printers' Ink.—Here the proportions of the first recipe are employed, but dammar is substituted for colophony.

The recipes given must depend on the quality of the raw materials used.

Differences in the resin and hydrocarbon can be corrected by alternating the proportion of lampblack present. The figures given above, however, are in most cases the best, and may be regarded as giving typical normal inks.

If other colours than black are required the proper amount of the suitable pigment is substituted for the lampblack. In order to manufacture a specially cheap ink resin oil may be substituted for the paraffin, and the colophony may be replaced by ordinary resin, Burgundy pitch or pine pitch. Fillings, used to increase the volume of the ink, can also be put in to a reasonable extent.

Gunther's Ink.

This is a black printers' ink which can also be used as an etching ground and a stamping colour. The ingredients are pitch or asphalt; the highest fractions of tar oil, or anthracene oil, after special preparation; spirit-soluble aniline, soft soap, that made with fish oil being the best for the purpose; and a drying Greenland fish oil.

These ingredients are mixed together at a temperature of 60° to 80° C.

To diminish the unpleasant smell of the green oil it is first prepared by being acted on by chlorine at a temperature of over 100° C., or by heating with an energetic oxidising agent such as nitric acid; then probably the amido bases are com-

bined and become less evil-smelling compounds than those originally existing as natural constituents of the green oil. The oil is then boiled with 5 per cent. of chloride of copper to deepen its brown colour. The following proportions have proved to be the best: 45 parts of green oil previously heated with chloride of copper, 40 of pitch or asphalt, 12 of soap, 5 to 8 of fish oil, according to the time of the year, and from 3 to 15 parts of spirit-soluble aniline dye in powder.

In an earlier patent Gunther protected the following process: The pigment ingredients are pitch or asphalt; rectified tar oil; mixtures of aniline violet with various fatty acids; and the fatty residue from the distillation of heavy resin oil; these materials are intimately mixed by being stirred together with heat and combine readily. The following proportions have been found to be good, but may be altered according to circumstances: 40 parts of asphalt, 28 of rectified tar oil, 8 of the fatty aniline violet, and 24 of the resin oil residue. If the mass is too thick it is diluted with more tar oil.

Still another patent of Gunther is concerned with the preliminary treatment of the heavy tar oil used in making these inks, and obtained as a residue in anthracene manufacture. The object of this treatment is to give the oil a brownish black colour, and the process consists in heating it with about 10 per cent. of chloride of copper which has previously been evaporated to get rid of its excess of acid. The chloride is then dissolved in warm water or stirred into the anthracene oil. This is then boiled until all the water has evaporated. The oil thus acquires a dark brown colour, and therefore requires a far smaller amount of aniline violet than would otherwise be necessary to give the required tint; $\frac{1}{5}$ per cent. of the dye-stuff is enough. The product then obtained can be substituted for the rectified tar oil and aniline violet and can be used without any addition as a stamping ink, especially for post-office work in cancelling postage stamps.

Dr. Artus's Ink.

Heat 60 kilos. of Venice pitch gently with 30 kilos. of oleic acid, as free as possible from stearine, and carefully rub the mixture up with 80 kilos. of soft soap. Then add 50 kilos. of calcined lampblack, first passed through a fine hair-sieve, and finally a solution of 40 kilos. of Prussian blue and 20 of oleic acid in 20 of water. Instead of the solution of Prussian blue indigo-carmine may be used, and of this 20 kilos. will be sufficient instead of the 40 of Prussian blue. The indigo-carmine must first be thoroughly rubbed up with water. Trials of this ink are said to have given very satisfactory results, and the ink is considered to be an improvement on Rösl's.

Rösl's Ink.

This consists of 9 parts of Austrian turpentine, 10 of soft soap, 4 of oleine, and 4 or more of lampblack. When these ingredients have been well mixed by the aid of heat they are thoroughly worked up in a paint mill, and the ink is then ready. The types are moistened and cleaned by means of a sponge dipped in a 1 per cent. solution of soda in water.

The advantages of this not very original ink in addition to its great divisibility, which allows it to be spread very thinly over the types, and therefore to give a very clear impression, are as follows: 1. It is easily made. 2. The cost of manufacture is one-third less, and the ink goes farther. 3. Its durability is such that it can be recovered from old printed matter by means of the above solution of soda, and the paper pulp can be bleached again for the manufacture of fresh paper by the same means. The ink also does away with the use of printers' lye, and also obviates the necessity of brushing the types. Hence they are not so quickly worn out as when ordinary inks are used.

Coal-Tar Inks.

Heat coal tar over a gentle fire and add, according to the degree of toughness to be produced, from 6 to 15 per cent. of colophony, raising the temperature until the resin is completely dissolved. Then stir into the mass 10 per cent. of paraffin oil, and pass the whole through a cloth or fine sieve. Then allow it to cool. Next correct the intense smell of the tar and paraffin by stirring in a mixture of bleaching powder and hydrochloric acid, until the chlorine evolved has destroyed the odour. About 300 grammes of acid are required for 50 of bleaching powder. The bleaching agents may also be advantageously added during the mixing of the ingredients, and the subsequent filtering will get rid of the residual bleaching powder. The disinfected vehicle is next heated, and is mixed slowly with constant stirring, with 20 to 25 per cent. of crude glycerine and 12 to 18 per cent. of lamp-black. The resultant paste is then rubbed up in a roller paint mill till it is thoroughly fine and uniform. In order to combine the glycerine better, and to get the desired deep black, bluish black or violet black ink, a little nigrosine, aniline blue or aniline violet is dissolved in the glycerine by heating on the water bath before it is added to the ink.

According to a supplementary patent, 100 kilos. of coal tar are gradually mixed with constant stirring with 2½ to 3 kilos. of sulphuric acid. The mass is then vigorously worked up, and gradually heated until it swells. When taken from the fire 1 kilo. of calcined soda is stirred in, and the stirring is kept up until the tar is nearly cold. Then from 2½ to 3 kilos. more of the soda are put in, and the mass is replaced on the fire and boiled until the tar froths strongly. It is then quickly removed from the fire and allowed to become quite cold.

It should be allowed to remain for a few days, and in the meantime it is disinfected with chlorine, either bubbled through it by means of a glass tube or generated in it by the addition of bleaching powder and hydrochloric acid. The black mass is then mixed with from $2\frac{1}{2}$ to 3 kilos. of lard and 4 to 5 kilos. of glycerine, or 8 to 10 of soap instead of glycerine, the whole being boiled together.

When the mass is thin, it is filtered through a cloth.

For finer inks, 2 to 5 kilos. of logwood extract in solution can be added to improve the black colour of the ink, and any required shade of deep black, blue black or violet black ink can be obtained by adding bichromate of potash, alum, tartar or copper solution. The filtered black ink is rubbed up with from $\frac{1}{10}$ to $\frac{1}{5}$ of lampblack. To still further improve the shade of black, a little aniline black, blue or violet, may be dissolved in the glycerine before it is mixed with the tar.

Schmidt Brothers' Ink.

Ordinary printers' ink consisting of lampblack and linseed oil can only be removed from paper with difficulty and never completely, for although the vehicle can be dissolved and removed the lampblack resists all chemical agents and solvents. Hence paper printed with such ink can never be remade into white paper again. To remedy this, the lampblack is replaced by other substances which can be removed by various chemical processes.

In order to make a removable ink, peroxide of manganese, a bye-product of many chemical industries, is employed, but other oxidised manganese compounds may be substituted, such as natural manganite and pyrolusite, with perfect success. The following is the recipe, which must be understood, however, to be variable according to the destined employment of the ink.

40 kilos. of the manganese compound are mixed with 60 of

boiled linseed oil, and finely rubbed up with it. The usual substitutes for linseed oil in printing ink manufacture, such as soft oleine soap, turpentine, glycerine, resin soap, etc., may be used instead, and the usual additions for producing a special tint, such as nigrosine, may be employed exactly as in ordinary inks. If paper printed with this ink is to be remade into white paper it is treated with cold or hot solution of carbonate of soda, and the whole is then rinsed to get rid of the ink. Any small traces of the manganese compound remaining can be removed with hyposulphite of soda. The remaining pulp is treated with acid or with the vapour of acid, hydrochloric being the best to use, as with the traces of manganese still left it develops chlorine, which helps to bleach the pulp.

Kircher & Ebner's Ink.

This is a similar ink to that of Schmidt Brothers, and the patent for it was taken out by Kircher in Austria, Germany and America fifteen years ago. It is prepared with sulphuretted hydrogen and compounds of iron, with the special purpose of securing an ink which should be removable, and allow the paper to be worked up over again. The State printing office of Vienna made experiments with it and obtained good results, but it never came into general use in Austria, and I know that the manufactory at Cannstatt had to shut down. Kircher employed the following processes:—

1. Dissolve a salt of iron in 6 times its bulk of clean water, and precipitate it with the sulphide. Wash the precipitate well, dry it quickly, and work it up with the vehicle in a paint mill.

2. Mix very fine iron filings with their chemical equivalent of sulphur, and fuse in a covered crucible at a gentle heat. Grind the cooled residue finely and mix with the vehicle.

3. Pass sulphuretted hydrogen over ferric oxide in a red-

hot tube until all action ceases. Mix the contents of the tube cold, and finely ground with the vehicle as before.

4. Reduce ferric or ferrous sulphate with carbon at not too high a temperature, and work the cold mass with the vehicle.

Iron Printing and Stamping Inks.

Ferric or ferrous salts, or metallic iron, are added to the printing or stamping inks made with lampblack and linseed oil; the iron combines intimately with the cellulose and size of the paper, and can be detected there even after all visible traces of ink have been removed.

Thenius's Ink.

Take 25 kilos. of linseed oil and 3 kilos. of fine litharge and boil until the oil thickens on cooling. Then allow it to settle. Melt also 10 kilos. of light American colophony, put it into the thickened oil, heat for a short time longer with 5 kilos. of coal-tar oil, and finally stir until cold. The coal-tar oil is made from the second fraction of the distillation of crude coal tar, and has a specific gravity of ·85 to ·89. The first distillate from the tar may also be used, mixed with the other, the two combined having a specific gravity of ·9. To make the oil from the mixture about 100 kilos. of it are put into a vat, lined with lead, with ½ kilo. of bichromate of potash, ½ kilo. of pyrolusite and 2 kilos. of pure sulphuric acid. The whole mass is stirred continuously for an hour, then allowed to stand for a few hours, and the darkened oil is poured off from the sediment, which contains the acid and many resinous bodies. The oil is washed first with warm water, and next with 2 per cent. of caustic soda-lye of 5° B., which frees it from large quantities of resinous impurities. The finished oil is thick, like honey, and is rubbed up with lampblack.

Or take 10 kilos. of fine, half-calcined oil lampblack, rub

it up very fine on the stone and add, gradually, rectified oil of turpentine until it becomes a thick paste, then continue rubbing until the mass acquires a lustre and is very fine. Mix with the same quantity of oil black like the first, but with the above coal-tar oil instead of turpentine. Rub on the stone 2 kilos. of fine Prussian blue to a very fine powder, and add to it ½ kilo. of powdered siccative, and a thick printers' varnish made from coal tar, so as to obtain the same thick consistency as before.

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